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ABSORPTION AND DESORPTION CURRENTS

The response of a linear system to a frequency dependent excitation can be transformed into a time dependent response and vice-versa. This fundamental principle covers a wide range of physical phenomena and in the context of the present discussion we focus on the dielectric properties ϵ' and ϵ'' . Their frequency dependence has been discussed in the previous chapters, and when one adopts the time domain measurements the response that is measured is the current as a function of time. In this chapter we discuss methods for transforming the time dependent current into frequency dependent ϵ' and ϵ'' . Experimental data are also included and where possible the transformed parameters in the frequency domain are compared with the experimentally obtained data using variable frequency instruments.

The frequency domain measurements of ϵ' and ϵ'' in the range of 10^{-2} Hz-10 GHz require different techniques over specific windows of frequency spectrum though it is possible to acquire a 'single' instrument which covers the entire range. In the past the necessity of using several instruments for different frequency ranges has been an incentive to apply and develop the time domain techniques. It is also argued that the supposed advantages of the time domain measurements is somewhat exaggerated because of the commercial availability of equipments covering the range stated above¹. The frequency variable instruments use bridge techniques and at any selected frequency the measurements are carried out over many cycles centered around this selected frequency. These methods have the advantage that the signal to noise ratio is considerably improved when compared with the wide band measurements. Hence very low loss angles of $\sim 10 \mu$ rad. can be measured with sufficient accuracy (Jonscher, 1983).

The time domain measurements, by their very nature, fall into the category of wide band measurements and lose the advantage of accuracy. However the same considerations of

accuracy apply to frequencies lower than 0.1 Hz which is the lower limit of ac bridge techniques and in this range of low frequencies, $10^{-6} < f < 0.1$ Hz, time domain measurements have an advantage. Use of time-domain techniques imply that the system is linear and any unexpected non-linearity introduces complications in the transformation techniques to be adopted. Moreover a consideration often overlooked is the fact that the charging time of the dielectric should be large, approximately ten times (Jonscher, 1983), compared with the discharging time. The frequency domain and time domain measurements should be viewed as complementary techniques; neither scheme has exclusive advantage over the other.

6.1 ABSORPTION CURRENT IN A DIELECTRIC

A fundamental concept that applies to linear dielectrics is the superposition principle. Discovered nearly a hundred years ago, the superposition principle states that each change in voltage impressed upon a dielectric produces a change in current as if it were acting alone. Von Schweidler^{2, 3} formulated the mathematical expression for the superposition and applied it to alternating voltages where the change of voltage is continuous and not step wise, as changes in the dc voltage dictate.

Consider a capacitor with a capacitance of C and a step voltage of V applied to it. The current is some function of time and we can express it as

$$i(t) = CV\phi(t) \quad (6.1)$$

If the voltage changes by ΔV_t at an instant T previous to t , the current changes according to the superposition principle,

$$\Delta i = C\Delta V_t \phi(t - T) \quad (6.2)$$

If a series of change in voltage occurs at times $T_1, T_2, \dots$ etc. then the change in current is given by

$$i = C \sum_N \Delta V_N \phi(t - T_N) \quad (6.3)$$

If the voltage changes continuously, instead of in discrete steps, the summation can be replaced by an integral,

$$i = C \int_{-\infty}^t \frac{dV(T)}{dT} \phi(t - T) dT \quad (6.4)$$

The integration may be carried out by a change of variable. Let $p = (t - T)$. Then $dp = -dT$ and equation (6.4) becomes

$$i = -C \int_0^{\infty} \frac{dV(t-p)}{dp} \phi(p) dp \quad (6.5)$$

The physical meaning attached to the variable p is that it represents a previous event of change in voltage. This equation is in a convenient form for application to alternating voltages:

$$v = V_{\max} \exp[j(\omega t + \delta)] \quad (6.6)$$

where δ is an arbitrary phase angle with reference to a chosen phasor, not to be confused with the dissipation angle. The voltage applied to the dielectric at the previous instant p is

$$v = V_{\max} \exp j[\omega(t - p) + \delta] \quad (6.7)$$

Differentiation of equation (6.7) with respect to p gives

$$\frac{dv}{dp} = -V_{\max} j\omega \exp j[\omega(t - p) + \delta] \quad (6.8)$$

Substituting equation (6.8) into (6.5) we get

$$i = j\omega CV_{\max} \int_0^{\infty} \exp j[\omega(t - p) + \delta] \phi(p) dp \quad (6.9)$$

The exponential term may be split up, to separate the part that does not contain the variable as:

$$\exp[j\omega(t - p) + \delta] = \exp[j(\omega t + \delta)] \times \exp(-j\omega p) \quad (6.10)$$

Equation (6.9) may now be expressed as:

$$i = \omega CV_{\max} \exp[j(\omega t + \delta)] \quad (6.11)$$

Substituting the identity

$$\exp(-j\omega p) = \cos(\omega p) - j \sin(\omega p) \quad (6.12)$$

we get the expression for current as:

$$i = \omega C V_{\max} \exp[j(\omega t + \delta)] \{ \int_0^\infty j \cos(\omega p) \varphi(p) dp + \int_0^\infty \sin(\omega p) \varphi(p) dp \} \quad (6.13)$$

The current, called the **absorption current**, consists of two components: The first term is in quadrature to the applied voltage and contributes to the real part of the complex dielectric constant. The second term is in phase and contributes to the dielectric loss.

An alternating voltage applied to a capacitor with a dielectric in between the electrodes produces a total current consisting of three components: (1) the capacitive current I_c which is in quadrature to the voltage. The quantity ϵ_∞ determines the magnitude of this current. (2) The absorption current I_a given by equation (6.13), (3) the ohmic conduction current I_c which is in phase with the voltage. It contributes only to the dielectric loss factor ϵ'' . The absorption current given by equation (6.13) may also be expressed as

$$i_a = j\omega C_0 V \epsilon_a^* = j\omega C_0 V (\epsilon_a' - j\epsilon_a'') \quad (6.14)$$

Equating the real and imaginary parts of eqs. (6.13) and (6.14) gives:

$$\begin{aligned} \epsilon_a' &= \epsilon' - \epsilon_\infty = \int_0^\infty \cos(\omega t) \varphi(t) dt \\ &= \frac{1}{C_0 V_0} \int_0^\infty i(t) \cos(\omega t) dt \end{aligned} \quad (6.15)$$

where C_0 is the vacuum capacitance of the capacitor and V_0 the applied voltage. Note that we have replaced p by the variable t without loss of generality.

$$\epsilon_a'' = \epsilon'' = \int_0^\infty \sin(\omega t) \varphi(t) dt \quad (6.16)$$

The standard notation in the published literature for ϵ_a' is $\epsilon' - \epsilon_\infty$ as shown in equation (6.15). Equations (6.15) and (6.16) are considered to be fundamental equations of dielectric theory. They relate the absorption current as a function of time to the dielectric constant and loss factor at constant voltage.

To show the generality of equations (6.15) and (6.16) we consider the exponential decay function

$$\phi(t) = Ae^{-t/\tau} \quad (6.17)$$

where τ is a constant independent of t and A is a constant that also includes the applied voltage V . Substituting this equation in equations (6.15) and (6.16) we have

$$(\varepsilon' - \varepsilon_\infty) = A \int_0^\infty e^{-t/\tau} \cos \omega t \, dt \quad (6.18)$$

$$\varepsilon'' = A \int_0^\infty e^{-t/\tau} \sin \omega t \, dt \quad (6.19)$$

We use the standard integrals:

$$\int_0^\infty e^{-px} \sin qx = \frac{q}{p^2 + q^2}$$

$$\int_0^\infty e^{-px} \cos qx = \frac{p}{p^2 + q^2}$$

Equations (6.18) and (6.19) then simplify to

$$\varepsilon' - \varepsilon_\infty = \frac{A\tau}{1 + \omega^2 \tau^2} \quad (6.20)$$

$$\varepsilon'' = \frac{A\omega\tau^2}{1 + \omega^2 \tau^2} \quad (6.21)$$

The factor A is a constant with the dimension of s^{-1} and if we equate it to

$$A = \frac{\varepsilon_s - \varepsilon_\infty}{\tau} \quad (6.22)$$

Equations (6.20) and (6.21) become

$$\varepsilon' = \varepsilon_\infty + \frac{(\varepsilon_s - \varepsilon_\infty)}{1 + \omega^2 \tau^2} \quad (6.23)$$

$$\varepsilon'' = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{1 + \omega^2\tau^2} \quad (6.24)$$

These are Debye equations (3.28) and (3.29) which we have analyzed earlier in considerable detail. Recovering Debye equations this way implies that the absorption currents in a material exhibiting a single relaxation time decay exponentially, in accordance with equation (6.17). As seen in chapter 5, there are very few materials which exhibit a pure Debye relaxation.

The transformation from the time domain to frequency domain using relationships (6.18) and (6.19) also proves that the inverse process of transformation from the frequency domain to time domain is legitimate. This latter transformation is carried out using equations

$$\phi(t) = \frac{2}{\pi} \int_0^\infty (\varepsilon' - \varepsilon_\infty) \cos \omega t d\omega \quad (6.25)$$

$$\phi(t) = \frac{2}{\pi} \int_0^\infty \varepsilon''(\omega) \sin \omega t d\omega \quad (6.26)$$

Substituting equations (6.20) and (6.21) in these and using the standard integrals

$$\int_0^\infty \frac{\cos mx}{x^2 + a^2} dx = \frac{\pi}{2a} e^{-ma}$$

$$\int_0^\infty \frac{x \sin mx}{x^2 + a^2} dx = \frac{\pi}{2} e^{-ma}$$

equation (6.17) is recovered.

A large number of dielectrics exhibit absorption currents that follow a power law according to

$$I(t) = Kt^{-n} \quad (6.27)$$

where K is a constant to be determined from experiments. Carrying out the transformation according to equations (6.15) and (6.16) we get

$$\varepsilon' - \varepsilon_\infty = \frac{K}{2} \omega^{n-1} \Gamma(1-n) \cos[(1-n)\pi/2]; \quad 0 < n < 1 \quad (6.28)$$

$$\varepsilon'' = K \omega^{n-1} \Gamma(1-n) \sin[(1-n)\pi/2]; \quad 0 < n < 2 \quad (6.29)$$

where the symbol Γ denotes the **Gamma function**. The left side of equation (6.28) is, of course, the dielectric decrement. For the ranges shown the integrals converge. The author has calculated⁴ ε' and $\tan \delta$ and fig. 6.1 shows the calculated values of the dielectric decrement and the loss factor versus frequency for various values of n , assuming $K = 1$. The power law (6.21) yields ε' that decreases with increasing frequency in accordance with dispersion behavior. However the loss factor decreases monotonically whereas a peak is expected.

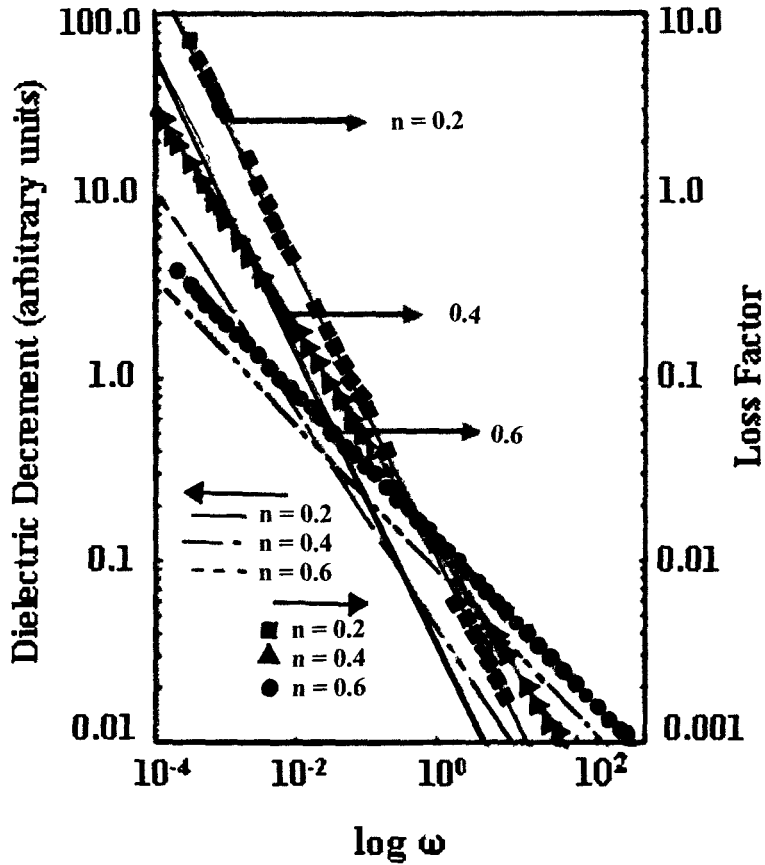


Fig. 6.1 The dielectric decrement and loss factor calculated by the author according to equation (6.28) at various values of the index n . The loss factor decreases with increasing n at the same value of ω (rad/s). The value of K in equations (6.28) and (6.29) is arbitrary.

Fig. 6.2 shows the shape of the loss factor versus $\log \omega$ for various values of n in the range of $0.5 \leq n \leq 2$.

In this range we have to use a different version of the solution of eq. (6.14) and (6.15)⁵ :

$$\int_0^{\infty} x^{p-1} \sin ax \, dx = \frac{\pi \sec \frac{p\pi}{2}}{2a^p \Gamma(1-p)}$$

$$\int_0^{\infty} x^{p-1} \cos ax \, dx = \frac{\pi \operatorname{cosec} \frac{p\pi}{2}}{2a^p \Gamma(1-p)}$$

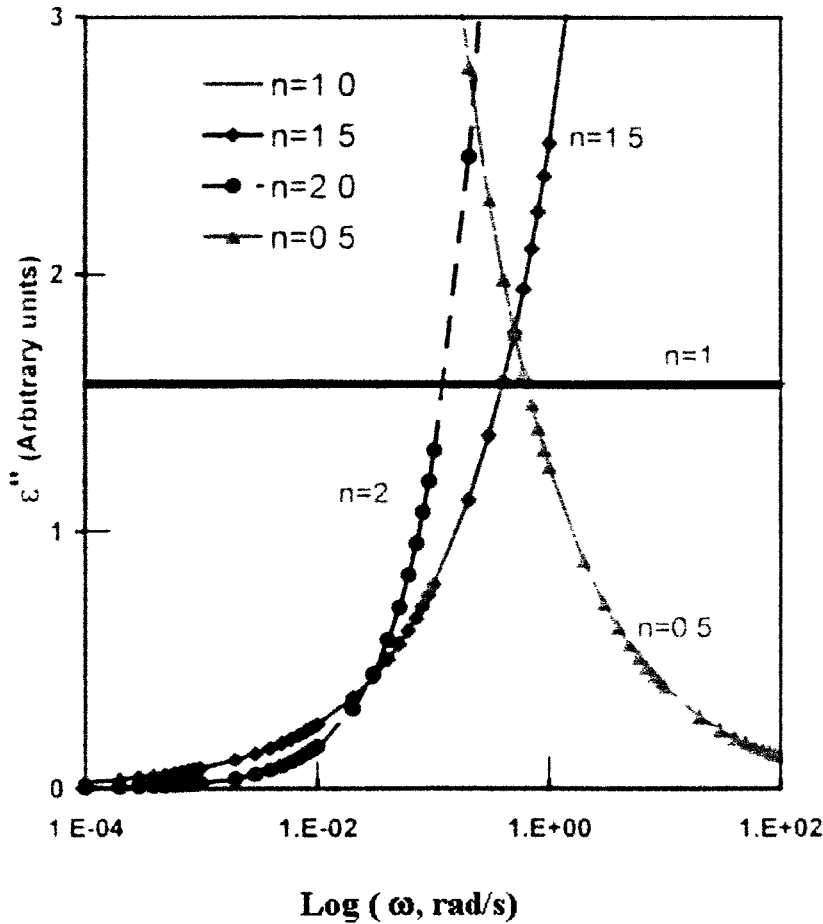


Fig. 6.2 Loss factor as a function of frequency at various values of $0.5 \leq n \leq 2.0$. ϵ'' is constant at $n = 1$. There is also a change of slope from negative to positive at $n > 1.0$.

The slope of the loss factor curve depends on the value of n in the range $1 < n < 2$ is positive, in contrast with the range $0 < n < 1$. The loss factor decreases, remains constant or increases according as n is lower, equal to or greater than one, respectively. The calculated values do not show a peak in contrast with the measurements in a majority of polar dielectrics and one of the reasons is that the theory expects the current to be infinite

at the instant of application of the voltage. Further the current cannot decrease with time according to the power law because if it does, it implies that the charge is infinite. The loss factor should be expressed as a combination of at least two power laws. Jonscher (1983) suggests an alternative to the power law, according to

$$i(t) \propto \frac{1}{(\omega_{\max} t)^n + (\omega_{\max} t)^{1+m}} \quad (6.30)$$

According to this equation a plot of t versus $\log I$ yields two straight lines. The larger slope at shorter times is $-n$ and the smaller slope at longer times is $-1-m$. The change over from one index to the other in the time domain occurs corresponding to the loss peak in the frequency domain. An experimental observation of such behavior is given by Sussi and Raju . The change of slope is probably associated with different processes of relaxation in contrast with the exponential decay, equation (6.17) for the Debye relaxation.

Jonscher¹ suggests that the absorption currents should be measured for an extended duration till the change of slope in the time domain is observed. This requirement is thought to neutralize the advantage of the time domain technique.

Combining equations (6.15) and (6.16) we can express the complex permittivity as

$$\varepsilon^* - \varepsilon_{\infty} = \frac{1}{C_0 V} \ell I(t) \quad (6.31)$$

where C_0 is the vacuum capacitance and V is the height of the voltage pulse. ℓ is the symbol for Laplace transform defined as

$$\ell[F(t)] = \int_0^{\infty} \exp(-j\omega t) F(t) dt$$

6.2 HAMON'S APPROXIMATION

Let us consider equation (6.27) and its transform given by (6.29). If we add the component of the loss factor due to conductivity then the latter equation becomes

$$\varepsilon'' = \frac{\sigma_{dc}}{\omega \varepsilon_0} + K \omega^{n-1} \{\Gamma(1-n) \sin[(1-n)\pi/2]\} \quad (6.32)$$

Hamon⁷ suggested the substitution

$$\omega t_1 = \{\Gamma(1-n)\sin[(1-n)\pi/2]\}^{-1/n} \quad (6.33)$$

noting that the right side of this equation is almost independent of n in the range $0.3 < n < 1.2$. This leads to the expression

$$\varepsilon'' \cong \frac{i(0.63/\omega)}{\omega C_0 V} \quad (6.34)$$

The equation is accurate to within $\pm 5\%$ for the stated range of n , but it also has the advantage that there is no need to measure σ_{dc} .

6.3 DISTRIBUTION OF RELAXATION TIME AND DIELECTRIC FUNCTION

It is useful to recapitulate from chapter 3 the brief discussion of the distribution of relaxation times in materials that exhibit a relaxation phenomenon which is much broader than the Debye relaxation. Analytical expressions are available for the calculation of the distribution of the relaxation functions $G(\tau)$ considered there. To provide continuity we summarize the equations, recalling that α , β and γ are the fitting parameters.

6.3.1 COLE-COLE FUNCTION

$$G(\tau) = \frac{\sin \alpha \pi}{2\pi \cosh[(1-\alpha)\ln(\tau/\tau_0) - \cos \alpha \pi]} \quad (3.94)$$

6.3.2. DAVIDSON-COLE FUNCTION

$$G(\tau) = \frac{\sin \beta \pi}{\pi} \left(\frac{\tau}{\tau_0 - \tau} \right)^\beta, \quad \tau < \tau_0 \quad (3.95)$$

$$= 0 \quad \tau > \tau_0 \quad (3.96)$$

6.3.3 FUOSS-KIRKWOOD FUNCTION

The distribution function for this relaxation is given as:

$$G(\tau) = \frac{\delta}{\pi} \frac{\cosh(\frac{\delta\pi}{2}) \cosh(\delta s)}{\cos^2(\delta\pi/2) + \sinh^2(\delta s)}; s = \log(\omega / \omega_p) \quad (3.97)$$

6.3.4 HAVRILIAK-NEGAMI FUNCTION⁸

$$G(\tau) = \frac{1}{\pi} \frac{(\tau / \tau_H)^{\alpha\beta} \sin(\beta\theta)}{[(\tau / \tau_H)^{2(1-\alpha)} + 2(\tau / \tau_H)^{1-\alpha} \cos \pi(1-\alpha) + 1]^{\beta/2}}; \quad (6.35)$$

$$\theta = \arctan \left[\frac{(\omega\tau_H)^{1-\alpha} \cos(\alpha\pi/2)}{1 + (\omega\tau_H)^{1-\alpha} \sin(\alpha\pi/2)} \right] \quad (6.36)$$

It is necessary to visualize these functions before we attempt to correlate the results that are obtained by applying them to specific materials. We use the variable $\log(\tau / \tau_0)$. Fig. (6.3) shows calculated distributions for the range of parameters as shown. For the Cole-Cole distribution the relaxation times are symmetrically distributed on either side of $\log(\tau / \tau_0) = 1$ while the Davidson-Cole distribution (fig. 6.4) is not only asymmetrical but $G(\tau) = 0$ at $\log(\tau / \tau_0) = 1$.

The Fuoss-Kirkwood distribution (fig. 6.5) is again symmetrical but it should be noted that the ordinate here is $\text{Log}(\omega/\omega_p)$ and hence the height of the distribution increases in the reverse order of the parameter β . The Havriliak-Negami distribution involves two parameters, α and β , and to discern the trend in change of distribution function we compute the relaxation times at various values of α with $\beta = 0.5$, and at various values of β with $\alpha = 0.5$. Fig. 6.6 shows the results which may be summarized as follows: (1) As α is increased the distribution becomes more narrow and the function $G(\tau)$ will attain a higher value at $\log(\tau/\tau_H) = 1$ though there appears to be a change of characteristics as α changes from 0.2 to 0.4. (2) As β increases the peak height increases and the distributions become broader.

Fig. 6.6 shows the application of equation (6.35) to poly(vinyl acetate) PVAc which has been studied by a number of authors. We recall that PVAc is an amorphous polar polymer with $T_G \sim 30^\circ\text{C}$. Nozaki and Mashimo⁹ have measured the absorption currents and evaluated the Havriliak parameters through the numerical Laplace transformation technique. The present author has used their data to calculate $G(\tau)$ ⁴. The abrupt change of distribution function at T_G is evident. Whether this is true for other polymers needs to be examined.

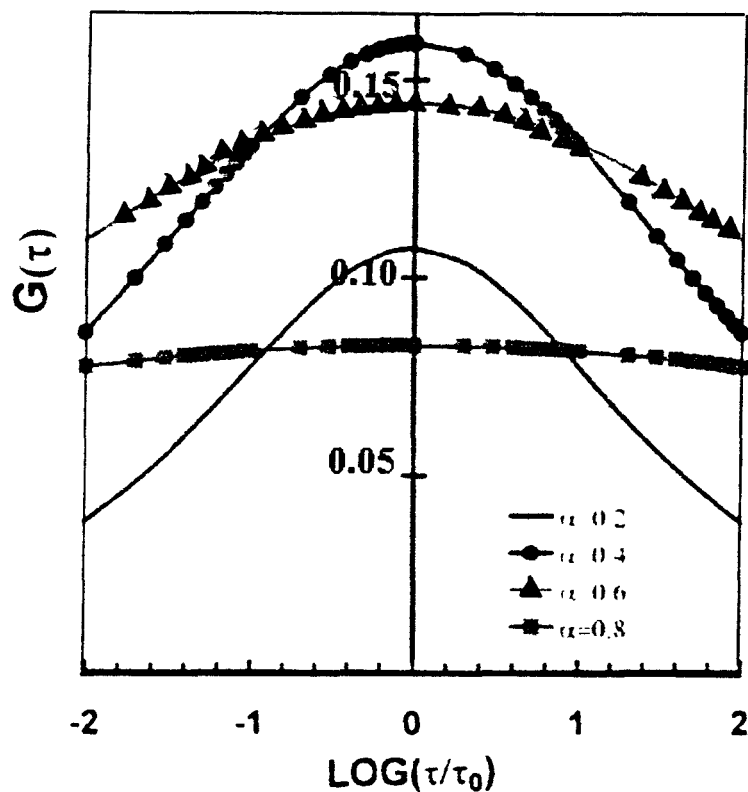


Fig. 6.3 Distribution of relaxation times according to Cole-Cole function (3.93). The distribution becomes broader with increasing value of α .

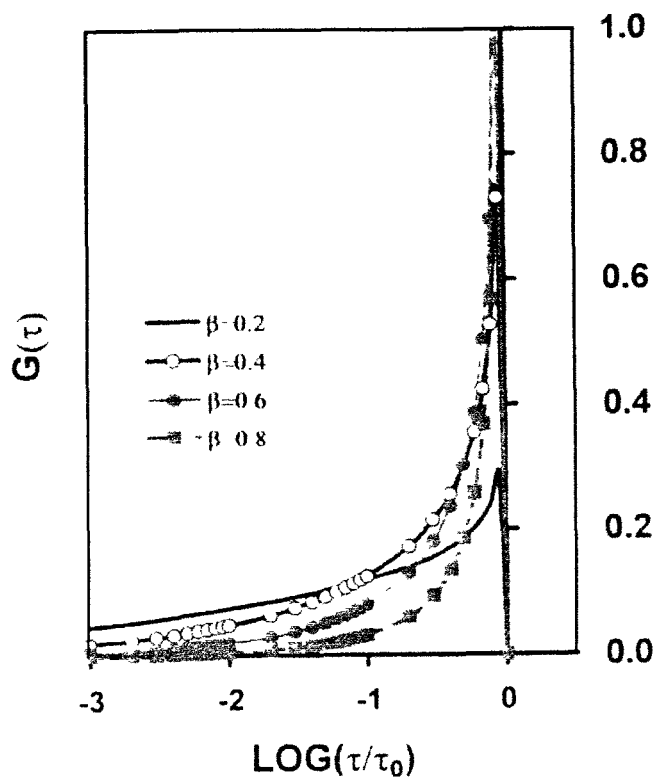


Fig. 6.4 Distribution of relaxation times according to Davidson-Cole function. $G(t) = 0$ for $t / t_0 > 1$.

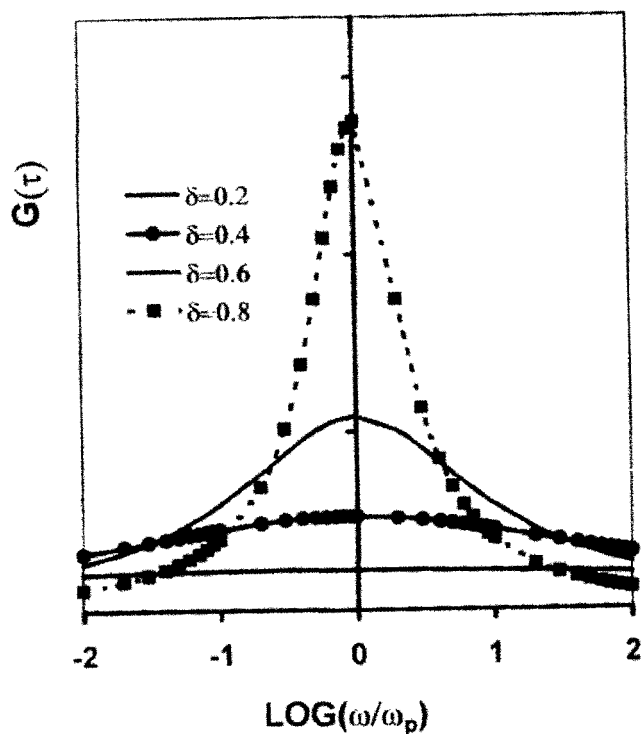


Fig. 6.5 Distribution of relaxation times according to Fuoss-Kirkwood relaxation, eq. (3.96). The distribution is symmetrical about $\omega = \omega_p$.

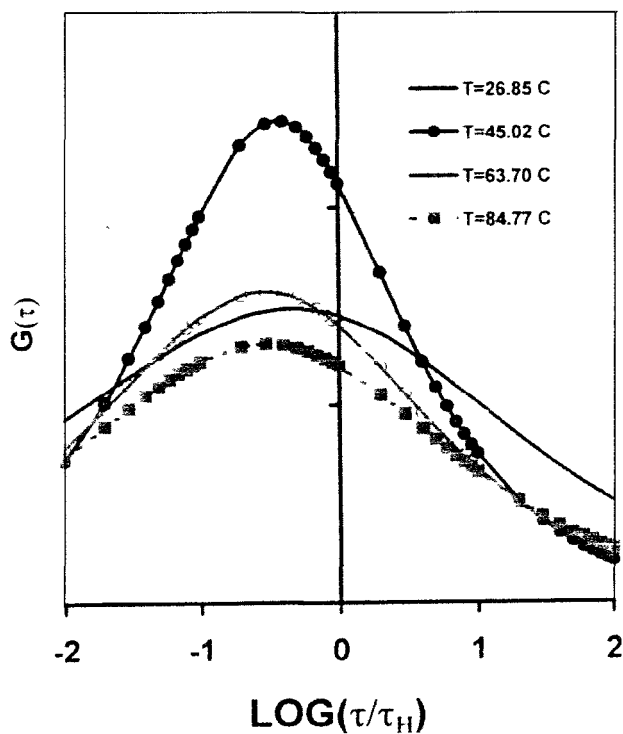


Fig. 6.6 Relaxation time in PVAc calculated by using the experimental results of Nozaki and Mashimo and values of α and β (1987). At T_g there is an abrupt change of $G(\tau)$.

6.4 THE WILLIAMS-WATTS FUNCTION

The detour to the distribution function of relaxation times was necessary due to the fact that it is an intermediate step in the numerical methods of transforming the time domain absorption currents to frequency domain dielectric loss factor. We shall, however, pursue the analytical methods a little further to indicate the potential and limitations of making approximations to facilitate the transformation. We have already seen that an exponential decay function for absorption current results in a Debye relaxation. A power law exhibits a peak, not necessarily Debye relaxation, in the dielectric loss factor. Williams and Watt suggested a decay function¹⁰, usually called the stretched exponential,

$$\phi(t) = \exp\left[-\left(\frac{t}{\tau_{w-w}}\right)^\gamma\right] \quad (6.37)$$

where $0 < \beta \leq 1$ and τ is an effective relaxation time. Sometimes this equation is called Kohlraush-Williams-Watts (KWW) equation because Kohlrausch used the same expression in 1863 to express the mechanical creep in glassy fibres (Alvarez et. al., 1991). For the time being we can drop the subscript for the relaxation time as confusion is not likely to occur. The complex dielectric constant is related to the decay function according to eq. (6.31)

$$\frac{\epsilon^* - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = \ell \left[-\frac{d\phi(t)}{dt} \right] \quad (6.38)$$

If the decay function is exponential according to Equation (6.37), or $\gamma = 1$ in equation (6.37), a reference to the Table of Laplace transforms gives

$$\frac{\epsilon^* - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = \frac{1}{1 + j\omega\tau} \quad (3.31)$$

which is the familiar Debye equation. Substitution of equation (6.37) in (6.38) yields

$$\frac{\epsilon^* - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = \ell \left[\frac{\gamma}{\tau_0} \left(\frac{t}{\tau_0} \right)^{-(1-\gamma)} \exp\left(-\left(\frac{t}{\tau_0}\right)^\gamma\right) \right] \quad (6.39)$$

The analytical expression for the Laplace transform of the right side is quite complicated. So we first substitute $\gamma = 0.5$ for which an analytical evaluation of the transform can be obtained as follows. For this special case equation (6.39) becomes

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \frac{1}{2} \left(\frac{\pi}{\tau_0} \right)^{1/2} \ell \left[\frac{1}{\sqrt{\pi t}} \exp - 2k(t)^{1/2} \right] \quad (6.40)$$

where $k = (\tau_0)^{-1/2}$. This has the standard form found in tabulated Laplace transforms¹¹ giving

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \frac{1}{2} \left(\frac{\pi}{\tau_0} \right)^{1/2} \frac{1}{(j\omega)^{1/2}} \exp\left(\frac{k^2}{j\omega}\right) \operatorname{erfc} \frac{k}{(j\omega)^{1/2}} \quad (6.41)$$

Substituting

$$\sqrt{j} = \frac{1}{\sqrt{2}} + \frac{j}{\sqrt{2}}$$

the transform (6.41) becomes

$$\begin{aligned} \frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} &= \sqrt{\pi} \frac{1-j}{\sqrt{8\omega\tau_0}} w(z); \\ z &= \frac{1+j}{\sqrt{8\omega\tau_0}}; w(z) = e^{-z^2} \operatorname{erfc}(-jz) \end{aligned} \quad (6.42)$$

The error function for complex arguments, $w(z)$, has been tabulated in reference¹². A sample calculation is provided here. Let $(\omega\tau_0) = 0.1$, $(\varepsilon_s - \varepsilon_\infty) = 2.0$, $\varepsilon_\infty = 2.25$. Then

$$\begin{aligned} z &= 1.12 + j1.12; \quad w(z) = 0.1957 \text{ (Abramowitz and Stegun, 1972);} \\ \frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} &= \sqrt{\pi} \times 0.1957 \times \frac{1-j}{0.894} = 0.39 - j0.39 \\ \varepsilon^* &= \varepsilon' - j\varepsilon'' = 3.03 - j1.47; \quad \varepsilon' = 3.03, \varepsilon'' = 1.47 \end{aligned}$$

The function $w(z)$ may also be calculated for values close to 0.5 by interpolation because values for $\gamma = 1$ may also be calculated using the Debye expression. William-Watts have computed equation (6.42) for several polymers including PVAc and obtained reasonable agreement between the measured and calculated values of $\varepsilon''/\varepsilon''_{\max}$ and $(\varepsilon' - \varepsilon_\infty) / (\varepsilon_s - \varepsilon_\infty)$ versus $\log(\omega/\omega_{\max})$.

The Laplace transform of equation (6.40) for other values of $0 < \gamma \leq 1$ has been given as a summation by Williams et. al.¹³

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \sum_{n=1}^{\infty} (-1)^{n-1} \frac{1}{(\omega\tau_0)^{n\gamma}} \frac{\Gamma(n\gamma + 1)}{\Gamma(n + 1)} [\cos(n\gamma\pi/2) - j \sin(n\gamma\pi/2)] \quad (6.43)$$

The range of parameters for which convergence is obtained is also worked out as

$$0.25 \leq \gamma \leq 1.0; \quad -1 \leq \log \omega\tau_0 \leq +4$$

Outside this range

$$0 \leq \gamma \leq 0.25; \quad -4 \leq \log \omega\tau_0 \leq +4 \quad \text{and}$$

$$0.25 \leq \gamma \leq 1.0; \quad -4 \leq \log \omega\tau_0 \leq -1$$

equation (6.43) was employed to calculate the real and imaginary parts separately. We then obtain the values of the following expressions:

$$\frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} \quad (\text{Dispersion Ratio})$$

$$\frac{\varepsilon''}{\varepsilon_s - \varepsilon_\infty} \quad (\text{Absorption Ratio})$$

We shall denote these ratios as the real part and imaginary part of the dielectric decrement ratio.

Watts et. al. employed a computer program to evaluate the equations (6.42) and (6.43). Their results are shown fig. 6.7.

The **dispersion ratios** plotted as a function of $\log(\omega\tau_0)$ changes approximately linearly for $\gamma = 0.1$ and the curves become steeper in the dispersion region as γ increases. The **absorption ratios** plotted as a function of $\log(\omega\tau_0)$ (fig. 6.8) exhibit the peak as the experimental results demand. In all cases $\log(\omega_{\max}\tau_0) < 0$. Though the absorption curves appear to be similar to Davidson-Cole functions the latter are found to be much broader.

The curves become narrower for higher values of γ , the Debye relaxation being obtained for $\gamma = 1$, satisfying equation (3.31).

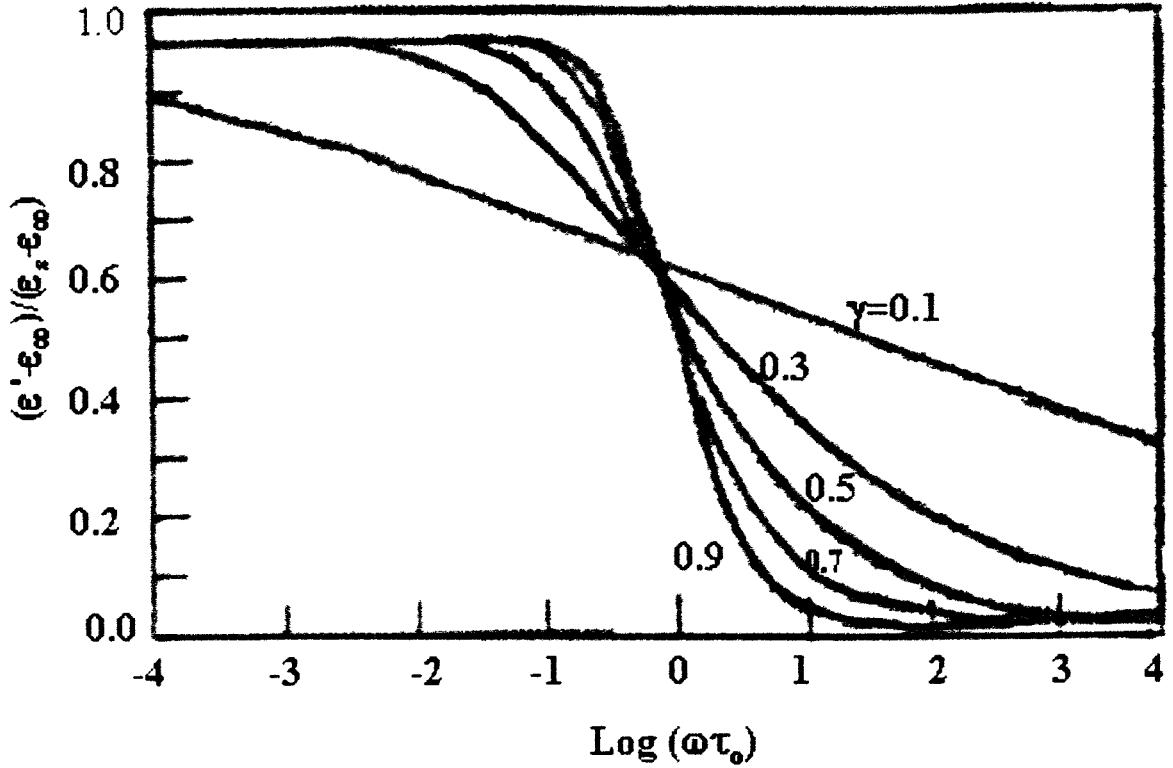


Fig. 6.7 Transformation from time domain to frequency domain using Laplace transform for odd values of the exponent, γ . The dispersion ratio, defined by the quantity shown on the ordinate (y-axis) is almost linear for small value of $\gamma = 0.1$. For higher values the familiar inverted S shape is generated (Williams et. al. 1971. with permission of the Faraday Soc.)

The half width of the absorption ratio curve may be used to determine the dielectric decrement ($\epsilon_s - \epsilon_\infty$) using the relation

$$(\epsilon_s - \epsilon_\infty) = k(\gamma) \Delta w \epsilon''_{\max} \quad (6.44)$$

where Δw is the half width of the absorption ratio curve and $k(\gamma)$ is a constant. For $\gamma = 1$ $k(\gamma) = 1.75$, and this corresponds to Fuoss-Kirkwood distribution.

The three parameters that appear in the Williams-Watt equation (6.31) are γ , τ and $(\epsilon_s - \epsilon_\infty)$. Numerical techniques are required to find the Laplace transform or evaluate the integrals. As an example, the function $\phi(t)$ is approximated to a series of exponentials¹⁴ and the Fourier transform of the resulting series is evaluated. The parameters γ and τ are fitted in terms of the peak and half-width of the dielectric loss function. The

approximations for each value of γ require determination of a large number of parameters (about 30) by curve fitting techniques. A simpler method of calculating these parameters one by one has been proposed by Weiss et. al.¹⁵ in contrast with other methods that involve simultaneous evaluations of all the three parameters. The method is demonstrated to apply in PVAc yielding results that compare favorably.

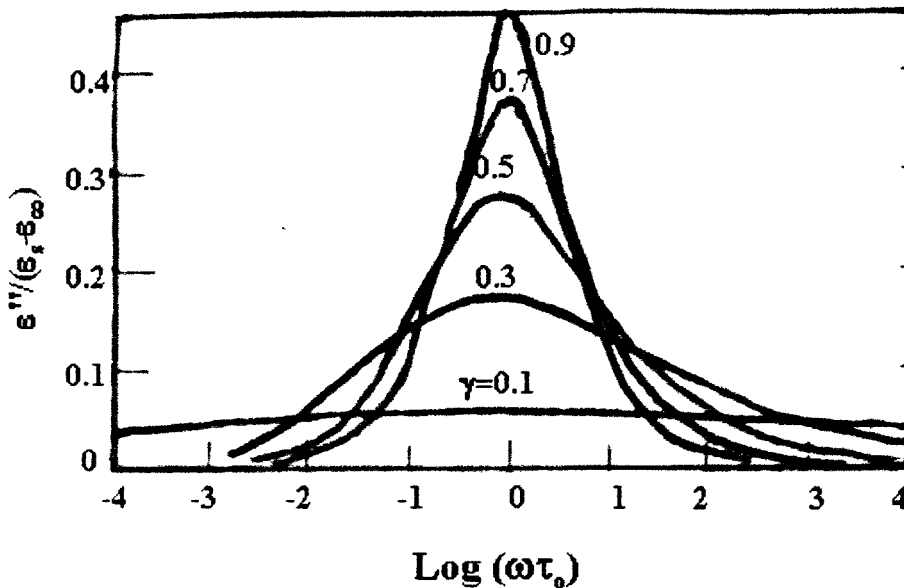


Fig 6.8 Transformation from time domain to frequency domain using Laplace transform for odd values of the exponent, γ . The absorption ratio, defined by the quantity shown on the ordinate (y-axis) is almost flat for small value of $\gamma = 0.1$. For higher values the familiar peak is observed (Williams et. al. 1971, with permission of Faraday Soc).

A summary for the function within square brackets in equation (6.38) is appropriate at this juncture from the point of view of using Laplace transforms for evaluating the dispersion ratios and absorption ratios. Let

$$\Psi(t) = -\frac{d\phi(t)}{dt} \quad (6.45)$$

Then the relaxation formulas yield the following time dependent functions:

A. DEBYE FUNCTION

$$\Psi(t) = \frac{1}{\tau} \exp\left(-\frac{t}{\tau}\right) \quad (6.46)$$

B. COLE-COLE FUNCTION

$$\Psi(t) = \frac{1}{\tau \Gamma(1-\alpha)} \left(\frac{t}{\tau} \right)^{-\alpha} ; \quad \text{for } \left(\frac{t}{\tau} \right) \ll 1 \quad (6.47)$$

$$\Psi(t) = \frac{(1-\alpha)}{\tau \Gamma \alpha} \left(\frac{t}{\tau} \right)^{\alpha-2} ; \quad \text{for } \left(\frac{t}{\tau} \right) \gg 1 \quad (6.48)$$

C. DAVIDSON-COLE FUNCTION

$$\Psi(t) = \frac{1}{\tau \Gamma \beta} \left(\frac{t}{\tau} \right)^{\beta-1} \exp \left(-\frac{t}{\tau} \right) \quad (6.49)$$

D. WILLIAMS AND WATTS FUNCTION

$$\Psi(t) = \frac{1}{\tau \Gamma \gamma} \left(\frac{t}{\tau} \right)^{\gamma-1} \exp \left(-\frac{t}{\tau} \right)^{\gamma} \quad (6.50)$$

E. GENERAL FUNCTION

$$\Psi(t) = \int_{-\infty}^{\infty} G(\tau) \exp \left(-\frac{t}{\tau} \right) d\tau \quad (6.51)$$

This expression assumes a superposition of Debye processes for an incremental relaxation time $G(\tau)$ $d(\tau)$ and follows directly from equation (6.46). The physical significance of the superposition in the time domain and the frequency domain is explained by Fig. 6.9.

Fig. 6.10 shows the function $\Psi(t)$ as a function of (t/τ) for a constant value of the parameters $\alpha, \beta, \gamma = 0.5$. For the purpose of comparison the exponential decay and the power law decay are also shown. For short times $(t/\tau \ll 1)$ which correspond to high frequencies, the three functions, namely Cole-Cole, Debye-Cole and William-Watts, have the same dependence on time for chosen parameters. However for large values of t/τ the Davidson-Cole function drops off rapidly due to the exponential term while the decay according to William-Watt function is less sharp.

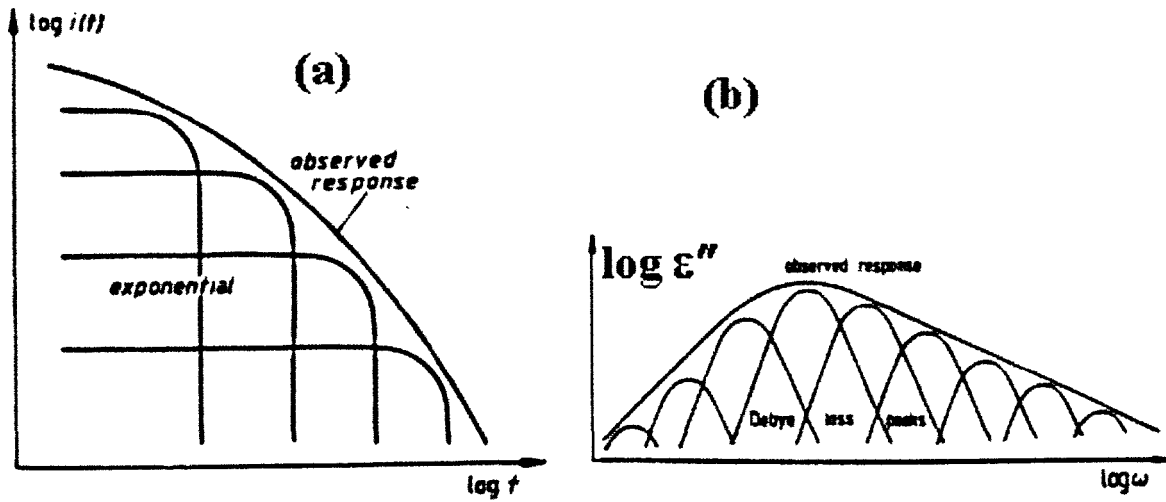


Fig. 6.9 Schematic illustration of superposition of (a) currents in the time domain, (b) loss factor in the frequency domain (Jonscher, 1983, with permission of Chelsea Dielectric Press).

6.5 THE $G(\tau)$ FUNCTION FOR WILLIAM-WATT CURRENT DECAY

Current measurements in the time domain give a single curve for a particular set of experimental conditions such as temperature and electric field. From these measurements the fitting parameters and τ are obtained using equations (6.46)-(6.50). From these parameters $G(\tau)$ is evaluated with the help of analytical equations (eqs. 3.94- 3.101). Using these values of τ , ϵ' and ϵ'' may be determined with the help of equations (3.89) and (3.90). However, it is not possible to express the $G(\tau)$ function analytically for the William-Watt decay function except for the particular value of $\gamma = 0.5$. In this case the expression for $G(\tau)$ is (Alvarez, 1991)

$$G(\tau) = \frac{1}{2} \pi^{-\frac{1}{2}} x^{-\frac{3}{2}} e^{-\frac{1}{4}x} \quad (6.52)$$

where $x = \tau / \tau_{ww}$. For other values of γ the expression for $G(\tau)$ is (Alvarez, 1991)

$$G(\tau) = -\frac{1}{\pi} \sum_{k=0}^{\infty} \frac{(-1)^k}{k!} \sin(\pi\gamma k) \frac{\Gamma(\gamma k + 1)}{x^{(\beta k + 1)}} \quad (6.53)$$

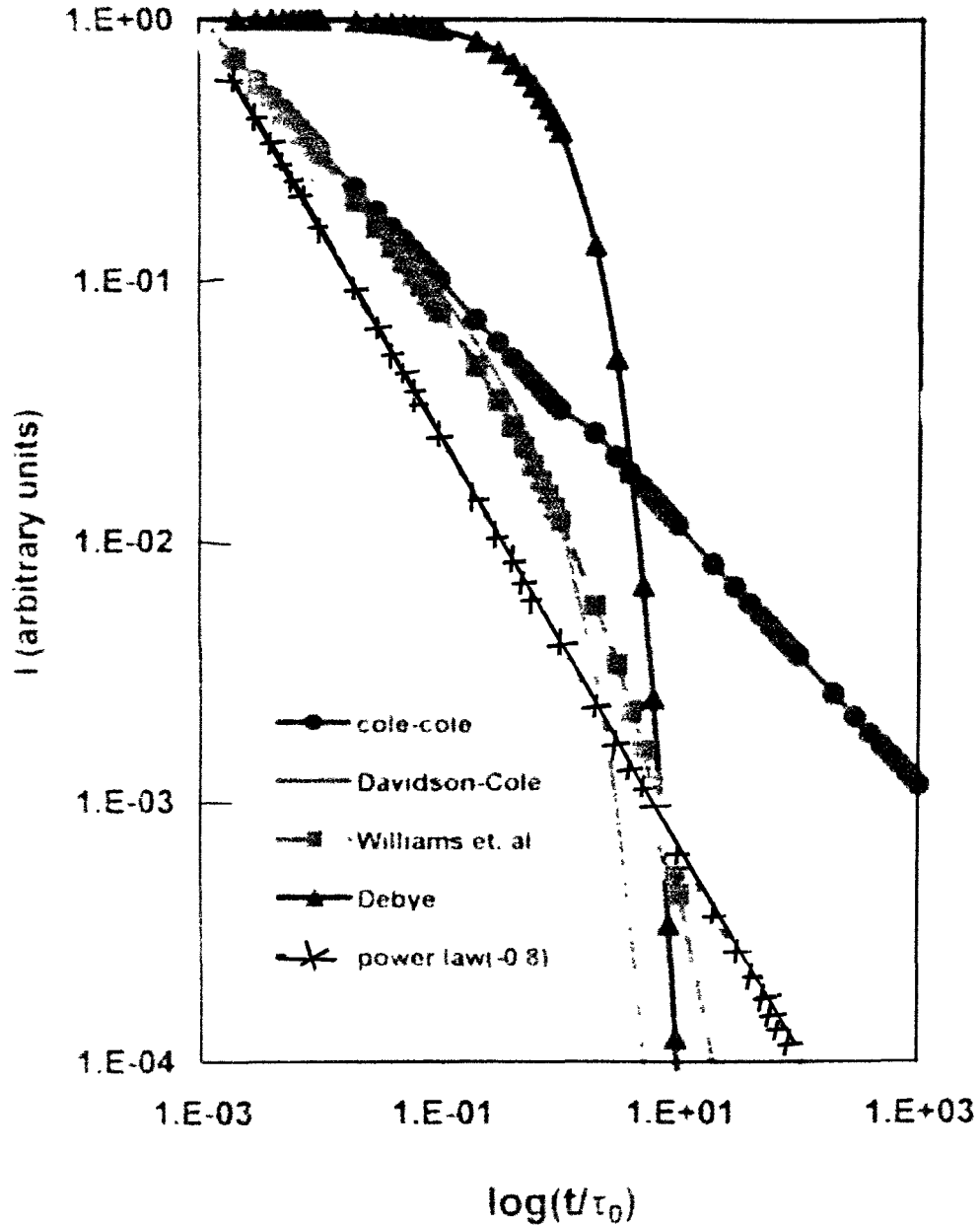


Fig. 6.10 Calculated current versus time for several relaxations, according to equations (6.46) – (6.50). 1-Cole-Cole, 2-Davidson-Cole, 3-Williams et. al., 4-Debye, 5- $t^{-0.8}$.

Though expression (6.53) is analytical its evaluation is beset with difficulties such as wide ranging alternating terms and large trigonometric functions. Hence, numerical techniques involving inversion of Laplace transform have been developed^{16, 17}.

Alvarez et. al. (1991) have also developed another important equation relating the William-Watt time domain parameter γ to the frequency domain parameters of Havriliak-Negami parameters, according to

$$\alpha\beta = \gamma^{1.23} \quad (6.54)$$

$$\ln \left[\frac{\tau_H}{\tau_{ww}} \right] = 2.6(1 - \gamma)^{0.5} \exp(-3\gamma) \quad (6.55)$$

where τ_H and τ_{ww} are the relaxation times according to Havriliak-Negami and William-Watt functions, respectively. Fig. 6.11 shows these calculated relationships. The usefulness of Fig. 6-11 lies in the fact that the values of (α, β) for a given value of γ is not material specific. Hence they have general validity and the transformation from the time domain to the frequency domain is accomplished as long as the value of γ is known.

We now summarize the procedure to be adopted for evaluating the dispersion ratio and the absorption ratio from the time-domain current measurements. For an arbitrary dependence of the current on time we use equation (6.38) and numerical Laplace transform yields the quantities $\epsilon' - \epsilon_\infty$ and ϵ'' . If the transient current is an analytical function of time, then $G(\tau)$ may be evaluated (section 6.3) and hence the quantity $(\epsilon_s - \epsilon_\infty)/(\epsilon_s - \epsilon_\infty)$ from equations given in section (3.16).

In chapter 5 enough experimental data are presented to bring out the fact that the α - and β - relaxations are not always distinct processes that occur in specific temperature ranges. As the temperature of some polymers is lowered towards T_G there is overlap of the two relaxations, (see Fig. 5.8 for three different possible ways of merging). For example in PMMA the α -relaxation merges with the β - relaxation at some temperature which is a few degrees above T_G ¹⁸. The β - relaxation occurs at higher frequencies than the α -relaxation, and it also has a weaker temperature dependency. It is present on either side of T_G .

In the merging region, two different ansatzes have been proposed for the analysis of dielectric relaxation. One is the simple superposition principle according to

$$\phi(t) = \phi_\alpha(t) + \phi_\beta(t) \quad (6.56)$$

where ϕ_α and ϕ_β are the normalized decay functions for the α - and β - relaxations respectively.

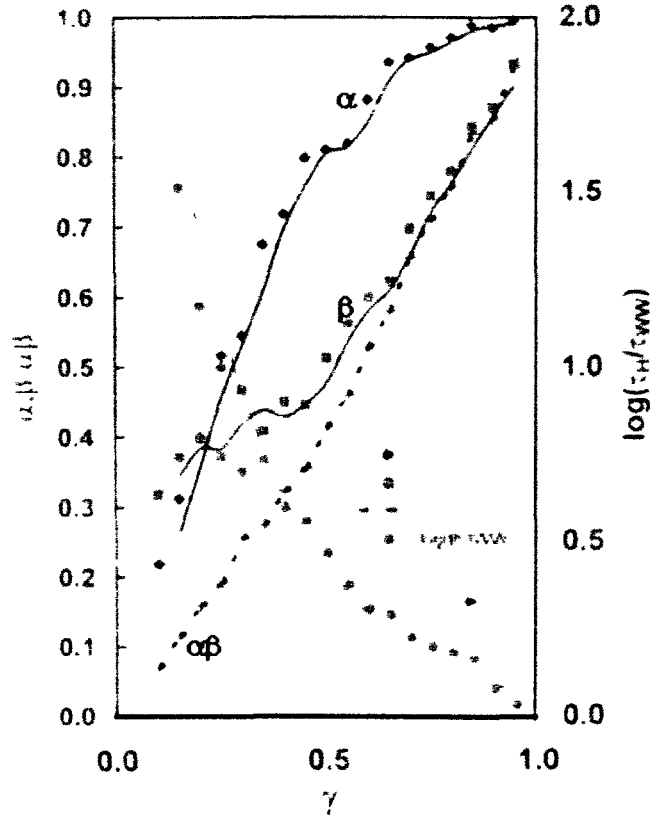


Fig. 6.11 Calculated relation between time domain parameters (γ) and H-N parameters (α , β), (Alvarez et. al., 1991, with permission of A. I. P.)

The normalized decay function is defined as

$$\text{at } t = 0 \quad \phi(t) = 1; \quad \text{at } t = \infty \quad \phi(t) = 0 \quad (6.57)$$

The second ansatz is called the **Williams ansatz** which is expressed as

$$\phi(t) = A\phi_\alpha t + (1 - A)\phi_\alpha(t)\phi_\beta(t) \quad (6.58)$$

where the individual decay functions are normalized according to equation (6.57). It is necessary to determine ϕ_α and ϕ_β at temperatures where the superposition from the other relaxation does not occur.

The relative merits of the superposition and the Williams ansatz in the merging region region of PMMA has been examined by Bergman et. al. (1998). The procedure adopted for transforming the frequency domain data into time domain current involves two steps:

- (1) Determine $G(\tau)$ from $\epsilon'' - \omega$ data by inverse Laplace transformation, eq. (3.90).
- (2) Determine $\phi_\alpha(t)$ and $\phi_\beta(t)$ from $G(\tau)$ according to equation (6.51).

(3) Determine $\phi(t)$ from equation (6.58).

Fig. 6.12 shows the result of step (1) above in PMMA, using broad band dielectric spectroscopy in the frequency range of $10^{-2} - 10^9$ Hz and temperature range of 220 - 490K. The loss factors from these measurements are shown in fig. (5-26). Fig. (6-13) shows the time domain currents. The current amplitude is seen to decrease with faster decay at higher temperatures.

A few comments with regard to numerical Laplace transformation is in order. Mopsik¹⁹ has adapted a cubic spline to the original data and uses the spline to define integration. The method is claimed to be computationally stable and more accurate. For an error of 10^{-4} or less, only ten points per decade are required for all frequencies that correspond to the measurement window. Provencher (1982) has developed a program called CONTIN for numerical inverse Laplace transformation, which is required to derive $G(\tau)$ from the KWW function. Imanishi et. al.²⁰ propose an algorithm for the determination of $G(\tau)$ from $\epsilon'' - \omega$ data.

6.6 EXPERIMENTAL MEASUREMENTS

The experimental arrangement for measurement of absorption currents is relatively simple and a typical setup is shown in fig. 6.14²¹. The transformation from the time domain to the frequency domain involves the assumption that the current is measured in the interval 0 to infinity, which is not attained in practice. The necessity to truncate the integral to a finite time t_{max} involves the assumption that the contribution of the integrand at $t > t_{max}$ ceases to contribute to ϵ' and ϵ'' ²². The lowest frequency at which ϵ' and ϵ'' are evaluated depends on the longest duration of the measurement and the current magnitude at that instant.

In the data acquisition system the measured current is converted from analog to digital and Shannon's **sampling theorem** states that a band limited function can be completely specified by equi-spaced data with two or more points per cycle of the highest frequency. The high frequency limit f_n is given by the time interval between successive readings or the sampling rate according to $2f_n = 1/\Delta t$. For example a sampling rate of 2 s^{-1} results in a high frequency cut off at 1 Hz. At high sampling rates a block averaging technique is required to obtain a smooth variation of current with time.

For low frequency data the current should be measured for extended periods and for a higher f_n the time interval should be smaller. These requirements result in voluminous data but the problem is somewhat simplified by the fact that the currents are greater at the beginning of the measurement.

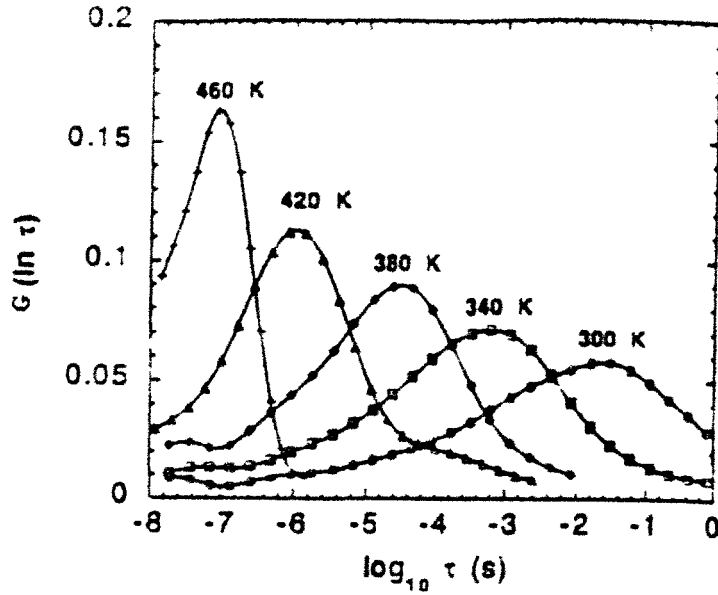


Fig. 6.12 The distribution of relaxation times at selected temperatures in PMMA derived from loss factor measurements. H-N function is used to calculate inversion from frequency domain data. The relaxation times decrease and the distributions become narrower as the temperature is increased (Bergman et. al., 1998, with permission of A. Inst. Phys.)

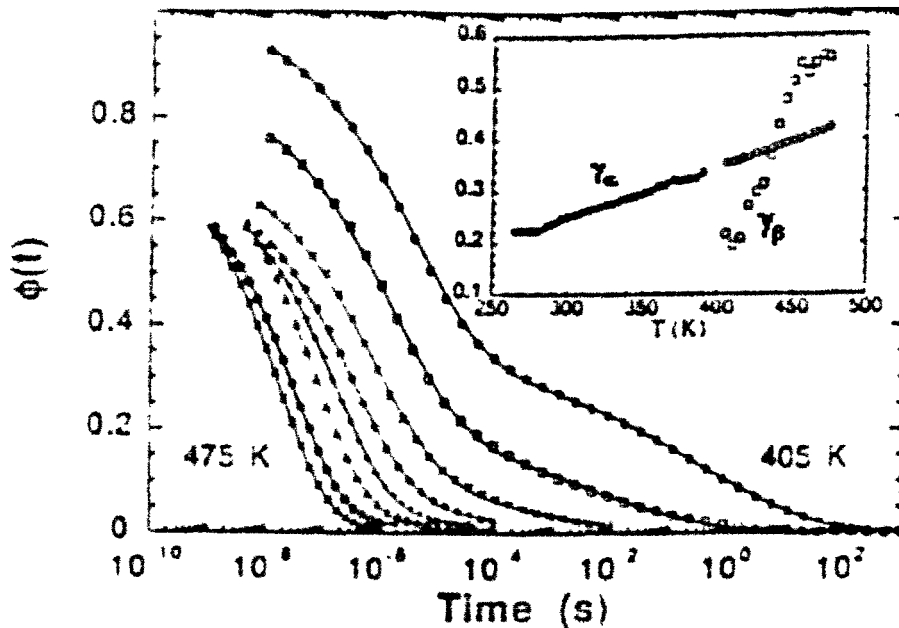


Fig. 6.13 Time domain current functions calculated using data shown in fig. 6.12. The temperature increases in steps of 10K. The inset shows the temperature dependence of the KWW stretching parameters for the α - and β - relaxations in PMMA (Bergman et. al. 1998, with permission of A. I. P.)

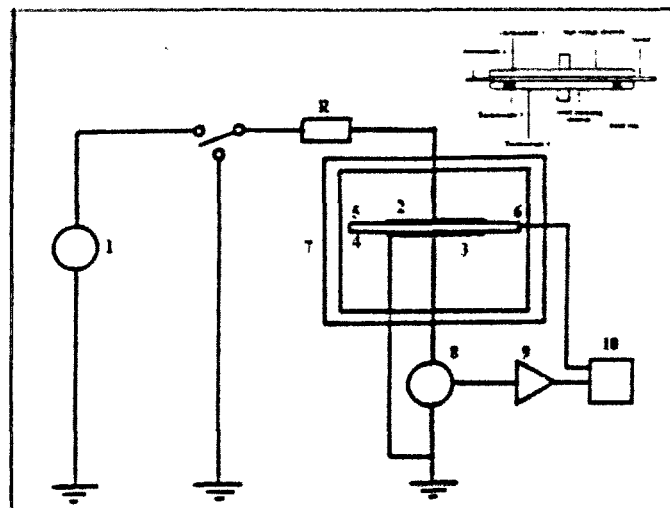


Fig 6.14 Schematic diagram for measuring absorption and desorption current. 1-variable DC supply, 2-High voltage electrode, 3-Measuring electrode, 4-Guard Electrode, 5-Sample, 6-Thermocouple, 7-Environmental chamber, 8-Electrometer, 9-Amplifier, 10-Recorder/computer. Inset shows details at the electrode (Sussi and Raju, 1994, with permission of Sampe journal).

The current may be obtained at greater intervals at later periods and the intermediate values obtained by interpolation. Quadratic schemes of interpolation have been found to be satisfactory except at short durations where the current decay is the steepest. In this range the $\log I(t)$ versus $\log(t)$ data are usually used for quadratic interpolation.

The sample under study is charged using a DC power source for the required time, a sensitive electrometer and recording equipment. The latter consists of a variable gain amplifier and A/D converter connected to a personal computer. The data acquisition system is capable of handling 16 channels of input with individual control for each channel. The frequency of sampling can be adjusted up to 4 kHz though after a few minutes of starting the experiment a much lower sampling rate is adequate to limit the volume of data. A block averaging scheme is employed with the number of readings in a block being related to the sampling rate.

6.6.1 POLY(VINYL ACETATE)

As already mentioned in the previous chapter PVAc is one of the most extensively investigated amorphous polymers, both in the frequency domain and the time domain providing an opportunity to compare the relative merits of the two methods over overlapping ranges of measurements. Table 6.1 lists selected publications.

Table 6.1
Dielectric Constant and Dielectric Loss Data in PVAc.

Authors & ref. No.	Year	Method	Temp. range °C	Frequency range (Hz)
Mead and Fuoss ²³	1941	F-D	50-100	60-10 ⁴
Broens and Muller ²⁴	1955	F-D	20-65	6-10 ⁷
Thurn and Wolf ²⁵	1956	F-D	-100 to 150	2×10 ⁶
Ishida et. al ²⁶	1962	F-D	- 61 to 150	5 - 10 ⁶
Saito ²⁷	1963	F-D and T-D	38.1-78.7	0.1-10 ⁶
Block, et. al.	1972	T-D	-	10 ⁻⁴ -1
Mashimo, et. al. ²⁸	1982	T-D and F-D	23.2-28.25	10 ⁻⁶ –10 ⁶
Weiss, et. al.	1985	T	66.7°C	502-7194
Nozaki and Mashimo ²⁹	1986	T-D & F-D	28-93	10 ⁻³ to 10 ⁷
Nozaki and Mashimo ³⁰	1987	F-D	26-85	10 ⁻⁶ –10 ⁶
Shioya and Mashimo ³¹	1987	T	26-85	6×10 ⁻⁵ -10 ⁶
Rendell et. al ³²	1987	T	26-85	10 ⁻⁷ to 10 ³
Murthy ³³	1990	T	26-85	10 ⁻⁶ –10 ⁶
Dionisio et. al. ³⁴	1993	F-D	45-70	16 - 10 ⁵

F - D = Frequency Domain, T - D = Time Domain, T = Theory

Other studies are due to Veselovski and Slutsker³⁵, Hikichi and Furuichi³⁶, Patterson³⁷, Sasabe and Moynihan³⁸, Funt and Sutherland³⁹.

Fig. 6.15 shows the complex dielectric constant in PVAc due to Nozaki and Mashimo (1986). The Havriliak-Negami distribution function is found to apply and the evaluated parameters α and β are shown in Table 6.2. In a subsequent publication Shioya and Mashimo (1987) have found that Cole-Cole distribution also applies well for the data.

The measured data have also been analyzed according to William-Watson function; while the agreement between the H-N parameters and the W-W parameter is good at lower frequencies, some differences prevail at the higher frequencies. This is attributed to a secondary relaxation process at higher frequencies, in addition to the main relaxation process. The secondary relaxation is thought to be due to side group rotation, the local mode relaxation of the main chain or co-operative relaxation of both motions.

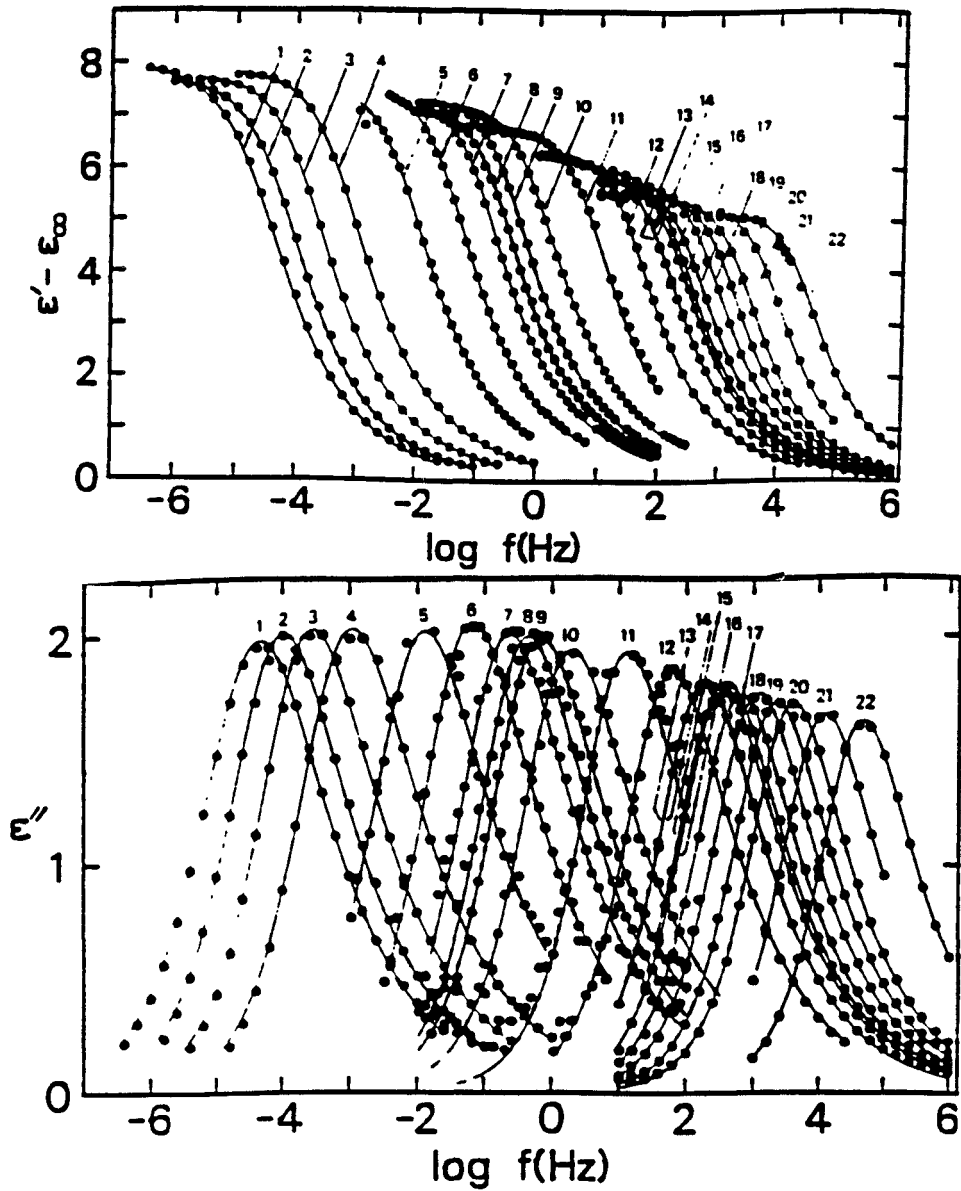


Fig. 6.15 Dispersion (a) and absorption (b) curves in PVAc at various temperatures: 1-26.8, 2-28.01, 3-29.41, 4-30.98, 5-34.95, 6-37.38, 7-40.20, 8-41.34, 9-42.3, 10-45.02, 11-50.20, 12-54.85, 13-58.80, 14-58.98, 15-61.23, 16-61.7, 17-63.70, 18-66.07, 19-68.91, 20-71.53, 21-77.62, 22-84.77 ($^{\circ}\text{C}$). Solid equation (Nozaki and Mashimo, 1987). (with permission of the A. Inst. Phy.)

We recall that the WLF equation holds true for many polymers at $T > T_G$. For PVAc this equation is found to hold true above 45°C (Nozaki and Mashimo, 1987), and the constants are given by

$$\log f_m = \frac{900.5}{T - 245.3} \quad (6.59)$$

At lower temperatures the WLF equation fails and the constants in this region are

$$\log f_m = -3.01 \times 10^4 \frac{1}{T} + 96.1 \quad (6.60)$$

This deviation from WLF equation is not observed if one evaluates the frequency at maximum loss according to W-W function (Mashimo et. al., 1982). The reasons are not quite clear if we suppose that the W-W function is a mathematical tool to specify the shape of the absorption currents. Equation (6.60) is Arrhenius law with an activation energy of 6 eV. At T_G the distribution of relaxation time shows an abrupt change as shown in Fig. 6.6.

Table 6.2
Dielectric Relaxation Parameters in PVAc [Nozaki and Mashimo, 1986].

T (K)	τ_0 (s)	$\Delta\epsilon$	ϵ_∞	α	β	μ (D)
301.25	5.70×10^3	7.922	3.139	0.390	0.821	2.458
301.71	2.94×10^3	8.017	3.138	0.388	0.813	2.490
302.90	9.25×10^2	8.053	3.135	0.402	0.819	2.515
303.60	4.90×10^2	7.960	3.133	0.414	0.822	2.498
305.80	5.64×10	8.040	3.126	0.421	0.823	2.549
309.16	1.86×10	7.279	3.117	0.450	0.860	2.367
311.15	3.26	7.444	3.111	0.445	0.844	2.440
315.65	1.20	6.800	3.098	0.467	0.864	2.298
326.64	7.16×10^{-3}	6.220	3.068	0.501	0.880	2.231
326.25	1.38×10^{-2}	6.004	3.068	0.513	0.856	2.161
330.47	4.15×10^{-2}	5.909	3.056	0.500	0.859	2.174
335.05	1.01×10^{-3}	5.582	3.043	0.526	0.868	2.110
339.30	3.26×10^{-4}	5.289	3.031	0.530	0.872	2.050
343.75	1.03×10^{-4}	5.197	3.018	0.551	0.869	2.060
349.80	3.02×10^{-5}	4.800	3.001	0.560	0.870	1.972
365.95	3.23×10^{-6}	4.170	2.955	0.590	0.873	1.865

$\Delta\epsilon = \epsilon_s - \epsilon_\infty$; (With permission of J. Chem. Phys.)

The last column in Table 6.2 is the dipole moment of the monomer according to Onsager's equation and the method of calculating it has been demonstrated in section 2.8.

Murthy (1990) has discussed the dielectric relaxation in PVAc and suggest that the deviation from the WLF equation may be removed if a power law is assumed instead of the WLF equation (5.19),

$$\log f_m = A\left[\frac{T - T_k}{T}\right]^s; \quad T > T_k \quad (6.61)$$

The large value of s (12.1 for PVAc) combined with the introduction of another arbitrary temperature T_k and lack of physical basis limits the usefulness of this equation.

6.7 COMMERCIAL DIELECTRICS

Absorption currents are measured, as described, during the application of a step voltage lasting from a few minutes to several hours. The recorded current is the sum of the polarization currents and conduction currents due to the electric field impressed. The absorption current is reversible; if the applied electric field is removed and the two electrodes are short circuited the current flows in the opposite direction and its magnitude is exactly equal to the absorption current. The conduction current, however, is not reversible, since the electric field is removed. To remove the effect of applied field on the absorption current the discharging current is preferably measured using the same setup shown in fig. 6.14. The discharging current is also called **desorption current**, though we use the common term “absorption current” to denote both charging and discharging conditions.

There are a number of reasons for the generation of absorption currents. These have been variously identified as⁴⁰:

- (1) electrode polarization,
- (2) dipolar orientation,
- (3) charge injection leading to space charge effects,
- (4) hopping of charge carriers between trapping sites, and
- (5) tunneling of charge carriers from the electrodes into the traps.

An attempt to identify the mechanism involves a study of the absorption currents by varying several parameters such as the electric field applied during charging, the temperature, sample thickness and electrode materials. Wintle⁴¹ has reviewed these processes (except the hopping process) and discussed their application to polymers. Table 6.3 summarizes the characteristics responsible for the transient currents.

The mechanisms of generation of absorption current in specific materials is still an active area of study and there is only agreement in the broad generality. Measurements to discriminate the various processes should include a systematic study of the influence of parameters such as field strength, electrode material, sample thickness, water content, temperature, and thermal history⁴². Indicators, which are looked for in experimental results, may be summarized as below:

Table 6.3

Summary of the characteristics of the mechanism responsible for transient currents. L is the thickness and F is the electric strength.

Process	field dependence of isochronal current	thickness dependence of isochronal current at constant field	electrode material dependence	Temperature dependence	time dependence $I \propto t^{-n}$	relation between charging and discharge transients
Electrode polarization	$\propto F^p$ where $p = 1$	not specified	strongly dependent through blocking parameter	thermally activated	initially $n = 0.5$ followed by $n > 1$	mirror images
Dipole orientation, uniformly distributed in bulk	$\propto F^p$ where $p = 1$	independent	independent	thermally activated	$0 \leq n \leq 2$	mirror images
Charge injection forming trapped space charge	related to mechanism controlling charge injection	independent	related to mechanism controlling charge injection	related to mechanism controlling charge injection	$0 \leq n \leq 1$	dissimilar
Tunneling	$\propto F^p$ where $p = 1$	L^{-1}	strongly dependent	independent	$0 \leq n \leq 2$	mirror images
Hopping	$\propto F^p$ where $p = 1$	independent	independent	thermally activated	$0 \leq n \leq 2$	mirror images

(Das-Gupta, 1997, with permission of IEEE).

1. Identical absorption and desorption currents, except in sign, implies that charge carriers are generated in the bulk and not injected from the electrodes. If dipolar processes are present, polymers as a rule exhibit a distribution of relaxation times with several overlapping processes. This is reflected as a change of slope of the power law index over short segments of time.
2. Oxidation of a polymer introduces additional dipoles of a different kind and these are likely to reside closer to the surface. The transient currents will then be inversely proportional to the thickness.
3. Charging current independent of the electrode material provides additional support for the absence of charge injection from the electrodes. Two different electrode materials with a large difference in work function may be employed in four different configurations to check the injection of charge carriers from the electrodes.

4. Independence of current on electrode material indicates lack of electrode polarization and the power law index for this process is close to 0.5.
5. Currents that are independent of thickness and temperature suggest that tunneling is at least not the principal mechanism for the transient current.
6. Hopping of ionic or electronic charge generally shows a transient decay of the discharging current divided in two successive domains having $n \sim 1$ and $n \sim 0$, respectively.
7. Presence of moisture generally reduces the activation energy for dipolar motions shifting the α -peak to lower temperatures. This is reflected in the absorption currents increasing at room temperature.

Lowell⁴³ has provided an analysis of the absorption and conduction currents by developing a model of the behavior of charges trapped on a polymer network. The theory is claimed to agree with experimentally observed current-time relationship in polymers.

6.7.1 ARAMID PAPER

Aramid Paper which is an aromatic polyamide is a high temperature insulating material and finds increasing applications in electrical equipment such as motors, generators, transformers and other high energy devices. There are a growing number of uses for this material in nuclear and space applications due to its excellent capability of withstanding intense levels of radiation such as beta, gamma and X-rays. The dielectric properties of this material are of obvious interest, and Sussi and Raju (1992) have measured the absorption currents covering a wide range of parameters.

To ensure repeatable results the samples were conditioned by heating for several hours (~ 5 hours) at high temperatures (~260°C). Two different electrode materials, aluminum and silver of 50 nm thickness, were vacuum deposited on the samples at reduced pressure of 0.1 mPa. A guard ring which was also vapor deposited was employed to reduce effects due to stray fields. Before each measurement a blank run was performed in order to free the sample from extraneous charges. This run consisted of raising the temperature of the sample at a constant rate to 200°C and short circuiting the electrodes for twelve hours. The influences of several factors on the absorption currents are described below.

A. TIME DEPENDENCE

Fig. 6.16 shows typical charging currents in a 127 μm thick sample at a temperature of 200°C and various poling electric fields for a time duration of 10^4 s. The charging currents decay very slowly and no polarity dependence is observed. There is no appreciable dependence of the current on the sample thickness or electrode material.

A similar slow time dependence of charging current has been reported for other insulating materials such as SiO_2 and SiO with aluminum electrodes⁴⁴, solid n-octadecane⁴⁵ and polycarbonate above its glass transition temperature of 150°C ⁴⁶. Lindmeyer suggests that a slow filling of traps by charge carriers in conjunction with a space charge effect is responsible for the slow decay of current with respect to time. It has also been suggested that a high electric field can induce traps in a polymer with the trap creation rate being proportional to the applied field. This theory, also, possibly explains the reason for not being able to observe a steady current under certain experimental conditions, even after as long as 10^5 s.

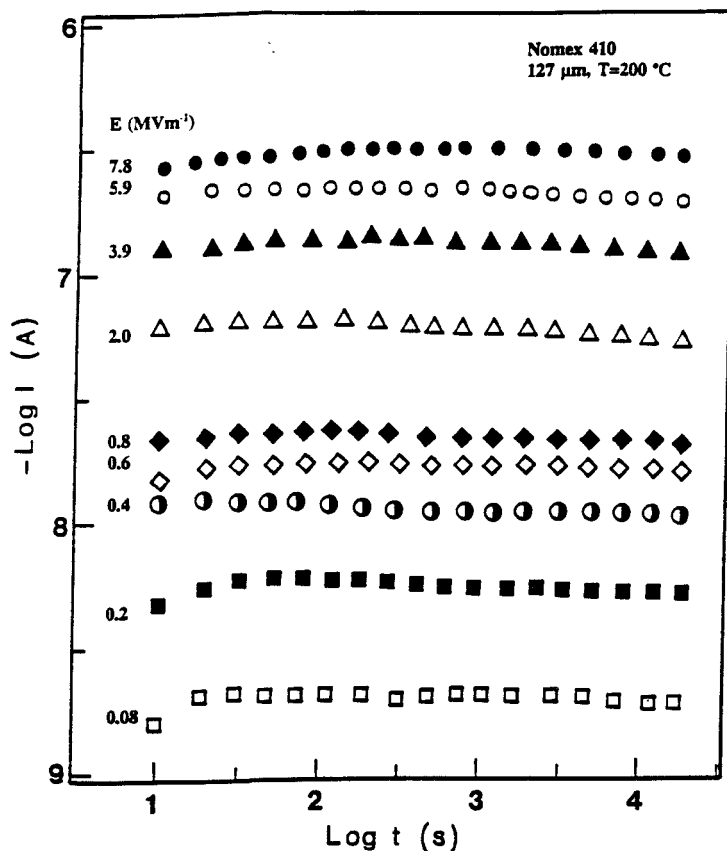


Fig. 6.16 Charging currents at various electric fields at 200°C in aromatic polyamide with silver electrodes. The current decays very slowly with time. This is just one of several types of decay of current in polymers (Sussi and Raju, 1992, with permission of Sampe journal).

Fig. 6.17 shows the influence of temperature on the absorption currents at a constant electric field. The decay of current is more rapid in the lower temperature range of $70 - 170^\circ\text{C}$. Such behavior has also been observed in linear polyamides in which the conduction currents in the range of $25 - 80^\circ\text{C}$ and $120 - 155^\circ\text{C}$ decay more rapidly than in the intermediate range of $80 - 110^\circ\text{C}$. Obviously there is a change of conduction mechanism above 150°C in aramid paper.

As stated earlier a comparison of charging and discharging currents permits reliable conclusions to be drawn with regard to the origin of charging current. Fig. 6.17 shows the discharging currents at 200°C after poling at various fields in the range of 0.08 – 8 MVm⁻¹. The current decays fast for a duration of about 10³ s where the power law holds with a value of n ~1.0. For times longer than 10³ s the current decay is much less pronounced and the decay constant in this range of time is between 0.1- 0.4.

The data in Figs. 6.17 and 6.18 clearly show that the charging and the discharging currents are dissimilar for times up to 10⁴s. Such dissimilarities have been observed in other polymers as well and there is no agreement on the processes responsible for them.

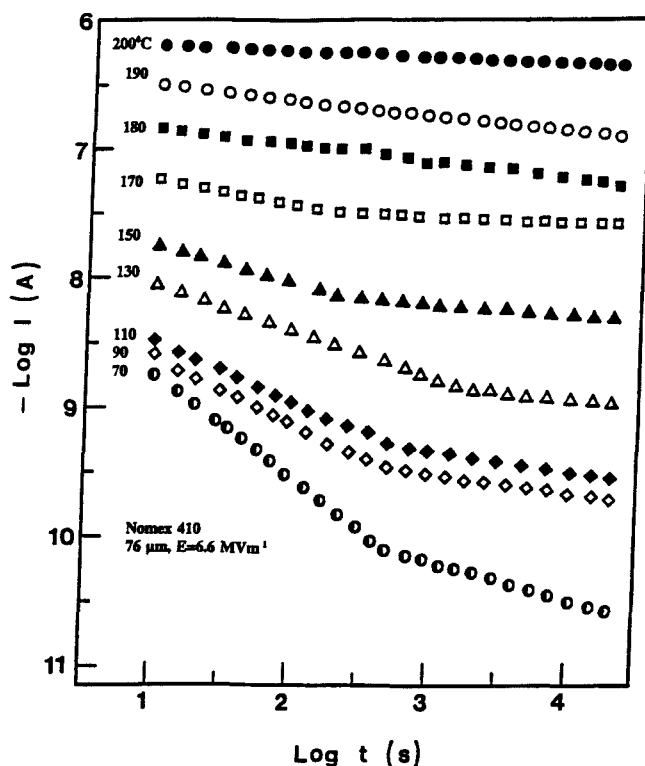


Fig. 6.17 Charging currents in aromatic polyamide at various temperatures and constant electric field of 6.6 MVm⁻¹ with silver electrodes. A change of mechanism is clearly seen above 150°C. (Sussi and Raju, with permission of Sampe Journal).

Lindmeyer (1965) discusses these dissimilarities with the aid of energy diagrams and attributed the initial transient during charging to empty traps. The current can be as large as allowed by the injecting barrier. As the traps become filled, the current reduces to the space charge limited current with traps. In the discharging period, on the other hand, the trapped carriers will be emptied towards both electrodes, the external circuit registering a smaller current.

Das Gupta and Brockley⁴⁷, on the other hand, concluded that the dissimilarity between the charging and discharging currents is due to the onset of quasi steady state conduction current which is superimposed on the transient current. If this reasoning holds good then the dissimilarity should increase with electric field or temperature.

It is relatively easy to interpret the results of fig. 6.18 in terms of the universal relaxation theory of Jonscher (chapter 4) who suggests that the time domain response of the current has two slopes or two values for the power law index, equation (6.30). An increase in the value of index at longer periods is attributed to a dipolar mechanism whereas a decrease at longer periods is attributed to interfacial polarization. On this basis it is suggested that the relaxation changes from dipolar to interfacial as the temperature is increased from 90°C to 200°C.

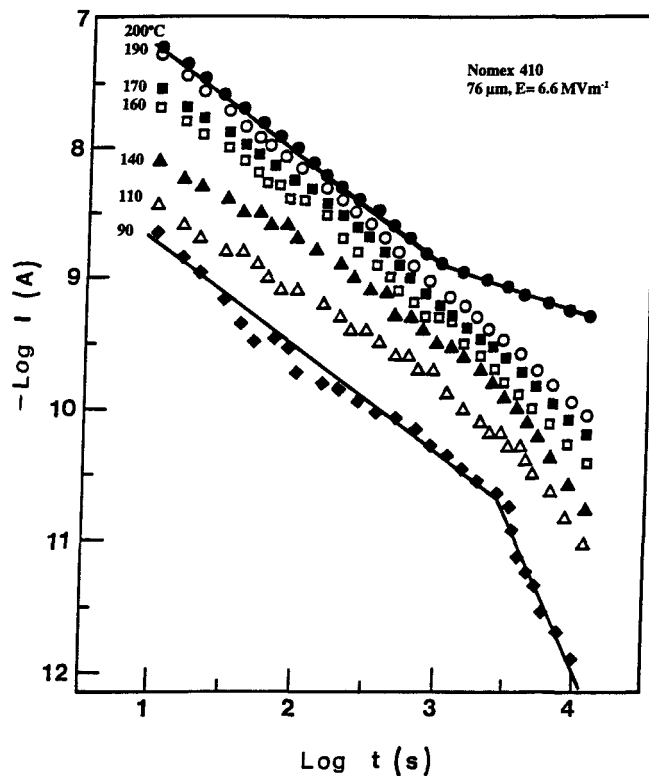


Fig. 6.18 Discharging currents at various temperatures and constant electric field of 6.6 MVm⁻¹ with silver electrodes. Charging and discharging currents are dissimilar indicating that dipolar processes are not dominant (Sussi and Raju, 1992, with permission of Sampe Journal).

Aramid paper is manufactured out of aromatic polyamide in the form of fibers which are amorphous and flocs (like corn flakes) which are crystalline, the finished product having a crystallinity of approximately 50%. The material abounds with boundaries between the crystalline and amorphous regions. Both the number of distributed trap levels and the mobility of charge carriers are likely to be higher resulting in a higher conductivity in

amorphous regions in comparison with the crystalline parts. This difference in conductivity is possibly the origin of the observed interfacial polarization.

B. TEMPERATURE DEPENDENCE

From Figs. 6.17 and 6.18 it is inferred that the isochronal discharging currents increase with temperature at the same electric field in the temperature range of 90 - 200°C. The currents show no significant peaks and from the slopes an approximate activation energy of 0.21 ± 0.05 eV may be evaluated.

C. FIELD DEPENDENCE

The isochronal charging current shows a linear relationship with the electric field at each temperature according to

$$I(t) = k(t)E^p \quad (6.62)$$

where k is a constant independent of E and p is approximately equal to one. Das-Gupta and Joyner⁴⁸ and Das-Gupta et. al.⁴⁹ have observed similar relationship in poly(ethylene terephthalate) (PET) at 173 K. The magnitude of isochronal current is observed to depend upon the time lapsed in contrast with aramid paper which shows only a marginal dependence on time. This difference is attributed to the fact that the charging currents vary slowly with time (Fig. 6.16).

D. EFFECT OF ELECTRODE MATERIAL

The charging currents are found to be dependent on the electrode material, silver yielding higher currents than aluminum. The power law index n is also higher for silver. However the discharging currents do not show any significant dependence on the electrode material.

E. LOW FREQUENCY DIELECTRIC LOSS FACTOR (ϵ'')

The theoretical basis for transforming the time domain data into ϵ'' -log ω has been dealt with in considerable detail in earlier sections of this chapter. The Hamon approximation given by equation

$$\epsilon'' \cong \frac{i(0.63/\omega)}{\omega C_0 V} \quad (6.34)$$

is easy to apply to the measured data. Fig. 6.19 shows the calculated values of ϵ'' at low frequencies in the temperature range of 100-190°C. Since dc conductivity contributes to the loss factor appropriate correction has been applied. Two peaks are observed at each temperature and they correspond to relaxation times of 1.6×10^3 s and 2×10^4 s. These values are comparable to the relaxation time of 1×10^4 s at 150°C obtained by Govinda Raju⁵⁰ from studies of thermally stimulated discharge currents in aramid paper. This study has shown that dipolar mechanism is responsible for the TSD currents in the temperature range cited and the observed peak at the higher frequency in fig. 6.19 (the first peak) is attributed to the dipolar mechanism. We also note that the low frequency peak (second peak) is more dominant at higher temperatures.

Sussi and Raju (1992) also examine whether the low frequency peak is possibly due to interfacial polarization according to the Maxwell Wagner equation, considering that the amorphous and crystalline regions have different conductivity. The parameters evaluated are shown in Table 6.3. Note the large increase of the loss factor at 200°C which is possibly due to an intensified Maxwell-Wagner effect. Higher temperatures increase the conductivity in amorphous regions more rapidly than in crystalline region. It is interesting to compare Fig. 6.19 with Fig. 5.17 which also demonstrates a large increase in ϵ'' as the temperature is increased.

6.7.2 COMPOSITE POLYAMIDE

The demand for electrically insulating polymers has increased over the years due to their high levels of electrical, chemical and mechanical integrity, making them ideally suited for several applications. Some organic polymers are capable of withstanding temperatures higher than 180°C and also have capability for withstanding radiation. The mechanical strength of aramid paper can be increased substantially for industrial applications by using it in conjunction with other polymers and such materials are referred to here as composites. For example an industrially available material is comprised of aramid-polyester-aramid (A-P-A) with three layers of equal thickness.

The isochronal currents measured by Sussi and Raju⁵¹ in A-P-A are shown in fig. 6.20 with regard to the influence of temperature on discharging currents. For each curve the current increases with temperature and shows a well defined peak in the range of 80-100°C. The position of this peak tends to shift to a higher temperature with decreasing times, suggesting the presence of thermal activation processes (Sussi and Raju, 1992). A comparison with fig. 6.16 shows that the observed peaks are due to the intermediate layer of polyester which has T_G in the vicinity of the observed peak. The dipolar contribution is suggested as a possible mechanism. Above 130°C the isochronal currents increase almost

monotonically with time and the increase is attributed to interfacial polarization as explained in the previous section.

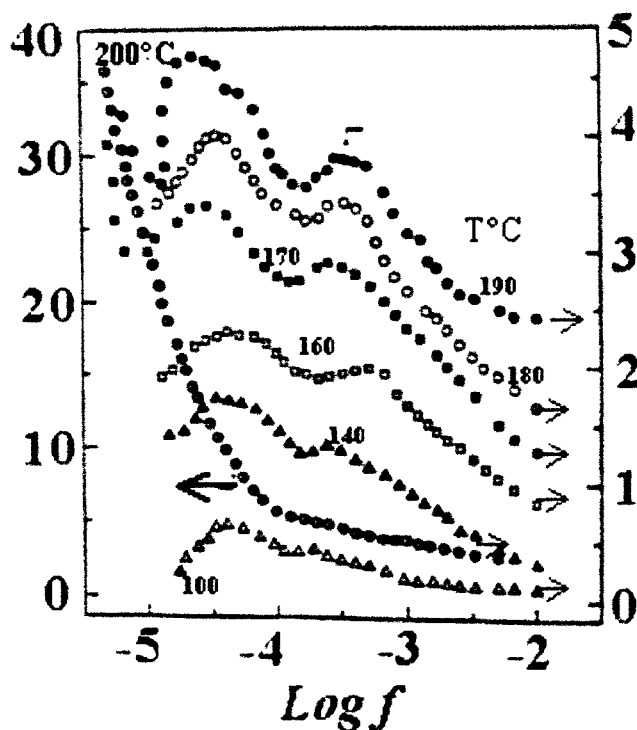
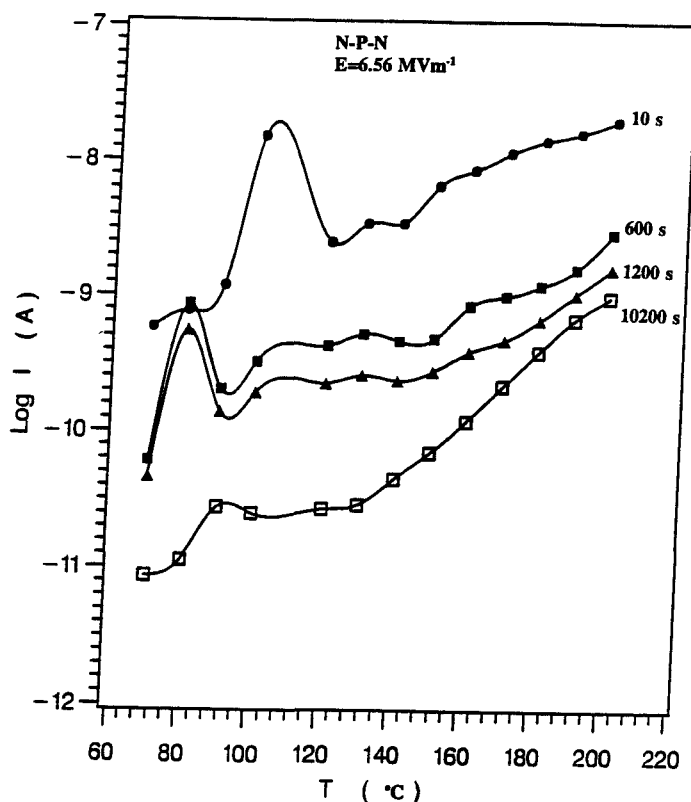


Fig. 6.19 Frequency dependence of dielectric loss factor ϵ'' at various temperatures. Pre-applied field of 6.6 MV m^{-1} ; charging time 5h; electrodes made of silver (Sussi and Raju, 1992). (with permission of Sampe Journal.)

Fig. 6.20 Temperature dependence of the isochronal discharge currents in composite aramid-polyester-aramid polymer at prescribed times. The electric field is 6.56 MVm^{-1} , $154 \mu\text{m}$ sample with aluminum electrodes. (Sussi and Raju, 1994: With permission of Sampe Journal)



6.7.3 POLY(ETHYLENE TEREPHTHALATE)

The absorption currents in PET have been measured by a number of authors. Das-Gupta and Joyner (1976) distinguish two temperature regions, 83-273K and 273-430K. In both regions the isochronal currents (I-T plots) are proportional to the electric field. No thickness dependence or electrode material dependence is observed. The charging and discharging transients are mirror images and two thermally activated energies of 0.65 and 1.6 eV are measured in the regions mentioned above respectively. The lower energy is identified with the β -relaxation and the higher energy with the α -relaxation.

Table 6.4

Loss factor in aramid paper (Sussi and Raju, 1992)

T (°C)	ϵ''	$\sigma (\Omega \text{ m})^{-1}$	τ (s)
(a) High frequency peak			
110	0.76	1.75×10^{-15}	1.6×10^3
130	1.14	5.48×10^{-15}	1.1×10^3
140	1.31	1.20×10^{-14}	6.3×10^2
150	2.14	2.62×10^{-14}	5.5×10^2
160	2.03	4.38×10^{-14}	3.1×10^2
(b) Low frequency peak			
110	0.89	7.0×10^{-16}	5.6×10^3
140	1.70	2.3×10^{-15}	5.0×10^3
160	2.27	4.0×10^{-15}	4.0×10^3

(with permission from SAMPE journal)

More recent results are due to Thielen et.al⁵² who discovered that the traditional use of three electrodes for measurement of current is likely to damage the ultra-thin films (<12-15 μm). This leads to spurious and noisy current, the preferred arrangement of electrodes being the simple two electrode system with lateral contacts. Fig. 6.21⁵³ shows the absorption current measurements and the power law index according to t^{-n} . While there is a slight but significant reduction in the current with increase of thickness, the index remains the same for all electric fields, $\sim 0.75 \pm 0.03$, which is close to the value for thicker films.

Isochronal currents for electric fields up to 50 MV/m showed that the current is ohmic in nature for short durations of 2-5 minutes whereas at longer durations (~ 210 min) the current increases exponentially. The electrode materials do not significantly influence the intensity and slope of the current. The transient current is attributed to the dipoles

whereas Schottky mechanism is found to hold true for the steady state current. Water content increases the steady state current more than it increases the transient current.

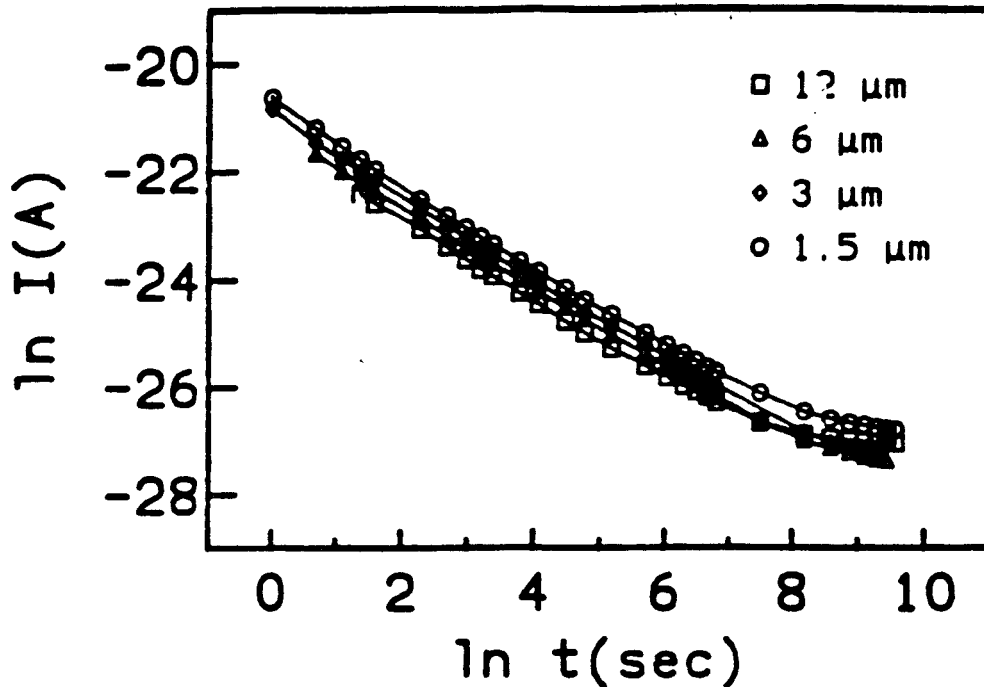


Fig. 6.21 Transient conductivity observed in Mylar™ films of various thicknesses (12, 6, 3 and 1.5 μm) for times ranging from 1 to 10^4 s $T=23^\circ\text{C}$, $\text{RH}=52\%$, $E_p=4\times 10^7$ V/m (Thielen et. al., 1994, with permission of American Inst. Phys).

There are two relaxation peaks observed in PET. The high temperature measurements covered by the Neagu et. al.⁵⁴ falls into the range $20\text{-}110^\circ\text{C}$ where both α - and β -relaxations are detected. In fact the β - relaxation is centered about -110°C ⁵⁵ and attributed to local motions of glycol methylene and carboxylic groups. It is characterized by a broad distribution. The dipoles corresponding to this relaxation are oriented in a short time $< 1\text{ s}$ and not measured by Thielen et. al (1994). The α -process is due to the motion of main chain and the distribution of relaxation times extends down to room temperature.

The measured current is probably due to this relaxation and the relaxation time in the range of $10^3\text{-}10^4$ s agrees with the expected value for this relaxation.

6.7.4 FLUOROPOLYMER

The fluoropolymer, commercially known as Tefzel™ (E. I. Dupont De Nemours & Co. Inc) is a copolymer of tetrafluoro-ethylene and ethylene considered as a high temperature insulating material. As far as the author is aware there is only one study carried out on

the dielectric properties (ϵ' and ϵ'') and absorption currents in this high temperature dielectric⁵⁶ and these data are presented below.

A. DIELECTRIC CONSTANT AND LOSS FACTOR

Fig. 6.22 shows ϵ' and ϵ'' as a function of temperature and frequency. The dielectric constant decreases with increasing temperature at each frequency. Further the loss factor shows a well defined peak in the region 100-120°C, the loss peak shifting to higher frequencies as the temperature is increased. These are characteristics of dipolar relaxation and plots of the molar polarizability versus $1/T$ (eq. 2.53) do not yield a straight line. It is evidence for the non-applicability of Debye theory for dipolar relaxation on the basis of a single relaxation time. This result is not surprising since most polymers are characterized by a distribution of relaxation times.

B. ABSORPTION CURRENTS

The absorption currents are measured at $5 \leq E \leq 40 \text{ MV m}^{-1}$ and $50^\circ \leq T \leq 200^\circ\text{C}$ by Wu and Raju (1965). Fig. 6-23 shows the time dependence of isothermal charging currents at 20 MVm^{-1} poling field and various temperatures. Results at other temperatures and electric fields shows a similar trend, suggesting that the mechanism for absorption current remains the same over these ranges of parameters. The material exhibits absorption currents that increase with time during the initial 1 – 100 s and then decrease slowly. Similar behavior is found in PE in which the conduction mechanism is identified mainly as space charge enhanced Schottky injection⁵⁷.

The absorption current also depends significantly on the electrode material, aluminum electrodes yielding higher currents than silver electrodes. This dependence suggests possible injection of charge carriers from the cathode and the accepted mechanism is field assisted thermionic emission. The current dependence on the electrode material can then be explained by the work function differences. Others have also reported similar results in PET and polyimide.

Injection of electrons from the cathode due to field assisted thermionic emission generally leads to a space charge layer within the thickness of the material and accumulation of charge carriers can also occur in the metal/polymer interface. The space charge, if sufficiently intense, will reduce the electric field at the cathode resulting in a decreased electron injection. The observed increase in current with time can only be explained on the basis of accumulation of positive charges within the polymer and close to the cathode. The ions originate within the bulk of the material or are injected from the anode and drift towards the cathode, thereby increasing the cathode field.

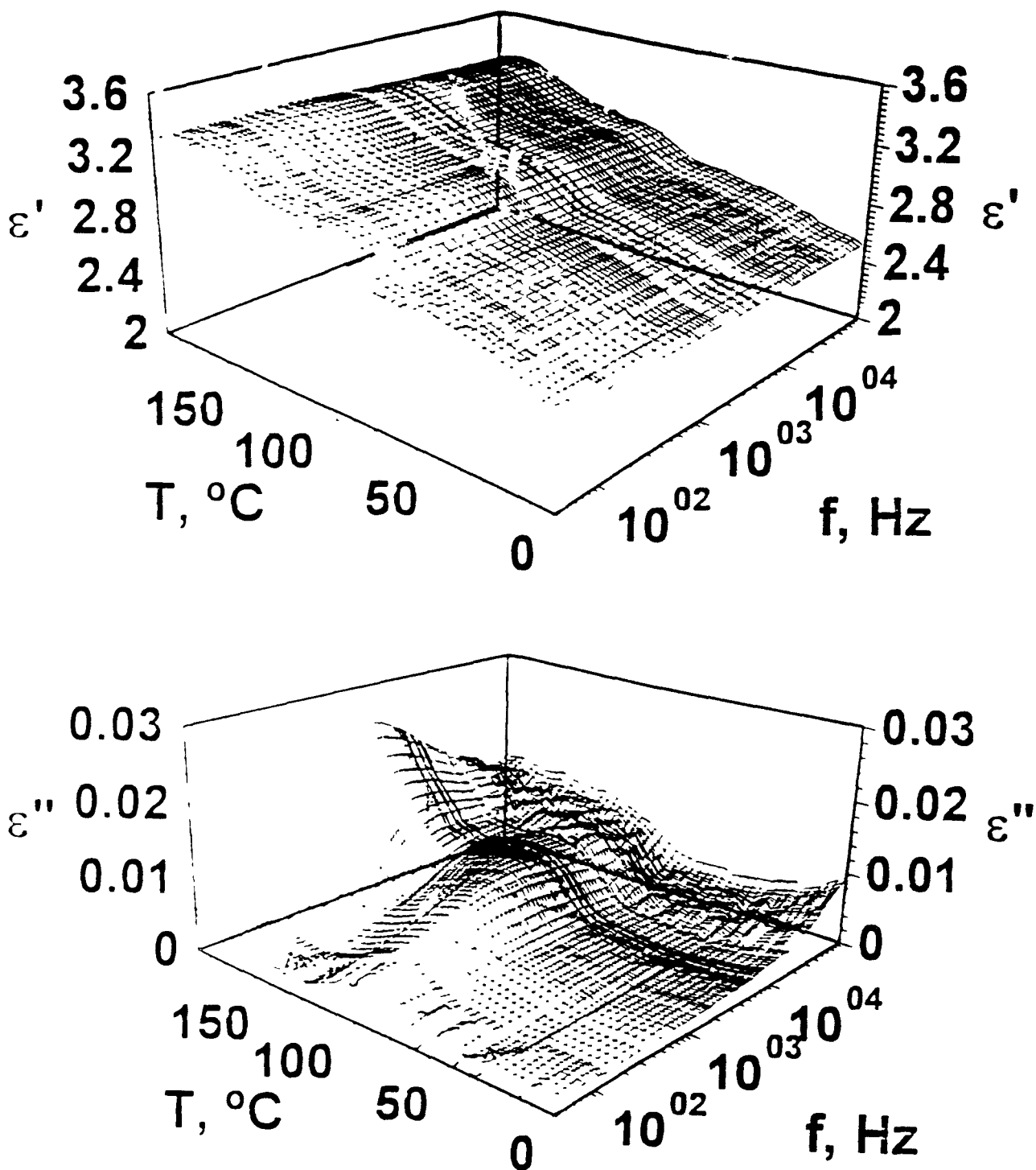


Fig. 6.22 Real and imaginary part of the complex dielectric constant in Tefzel (author's measurements).

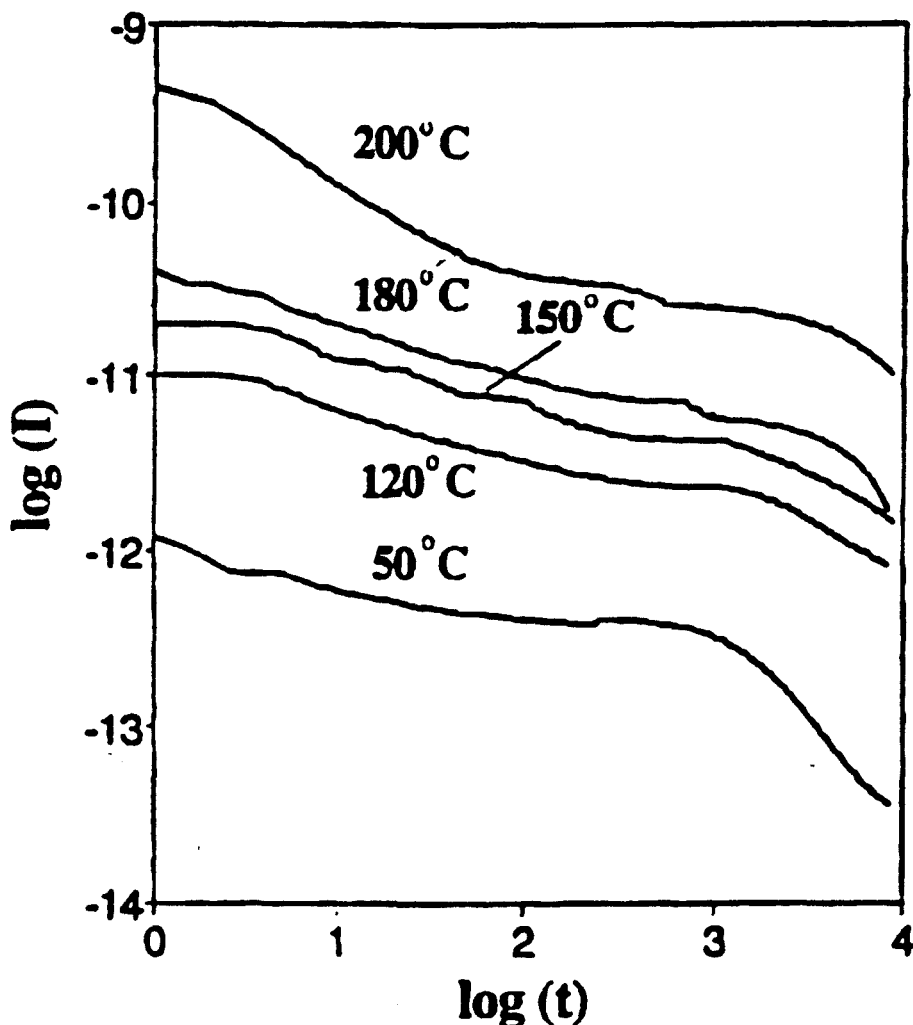


Fig. 6.23 Isothermal charging currents at 20 MV/m at various temperatures (electrodes silver) in fluoropolymer (Wu and Raju, 1995, with permission of IEEE).

There are several sources for ion generation. One of them is impurity ions, the current due to which tends to decrease if successive measurements are repeated on the same sample within a short interval of time. A second source of ions is due to autoionization of one of the atoms in the monomer, as demonstrated by Raju (1971) in aromatic polyamide. There is no experimental evidence in the literature to support this mechanism in this copolymer, and it is shown in chapter 7 that ionic conduction is not a feasible mechanism in this material.

Poole-Frenkel mechanism (Ch. 7) suggests that the electric field lowers the barrier for transition of charge carriers in the localized states. The mechanism is not specific to charge carriers of a specific type and is similar for donors (creating electrons) or acceptors (generating holes). Holes generated within the bulk drift towards the cathode and contribute to the intensification of the field.

An additional mechanism, which has been suggested to account for an increase in current with time, is the increase of the number of traps in the bulk due to the influence of the electric field. The new traps that are created permit more injection resulting in an increase of the current. Such an increase in the number of traps is likely to saturate after a certain time of application of voltage and the surface potential of the polymer is expected to vary according to fig. (6.23).

At longer time duration the current decreases with time and this is the more common behavior for many polymers. Lindmeyer [1965] suggests that gradual filling of traps by charge carriers leads to this type of behavior. Further the polymer-metal interface is sensitive to structural features such as the density of localized molecular states in the polymer and tunneling range of the delocalized electrons in the metal electrode. Unless the charge is moved away from the site of injection, further injection is reduced. This effect added to the bulk trapping causes decay of charging currents at longer periods.

Isothermal absorption currents are also measured by interchanging the polarity of the electrodes. The currents were approximately the same as the current under positive polarity fields (fig. 6.23). This is considered to be reasonable because both electrodes are vacuum deposited with the same type of metal under identical conditions and the change in surface conditions is not significant enough to cause a change in emission.

6.7.5 POLYIMIDE

Chohan et. al.⁵⁸ have measured the absorption and desorption currents in Kapton and the two currents were dissimilar in selected temperatures in the range 39°-204°C. Fig. 6-24 shows the low frequency loss factors versus the frequency, which exhibit peaks that shift to lower frequencies as the temperature decreases. This observation is attributed to the interfacial polarization either at the electrode-dielectric interface or in boundaries between crystalline and amorphous regions. There is need for systematic study of transient currents in this important polymer over a wider range of temperature and electric field.

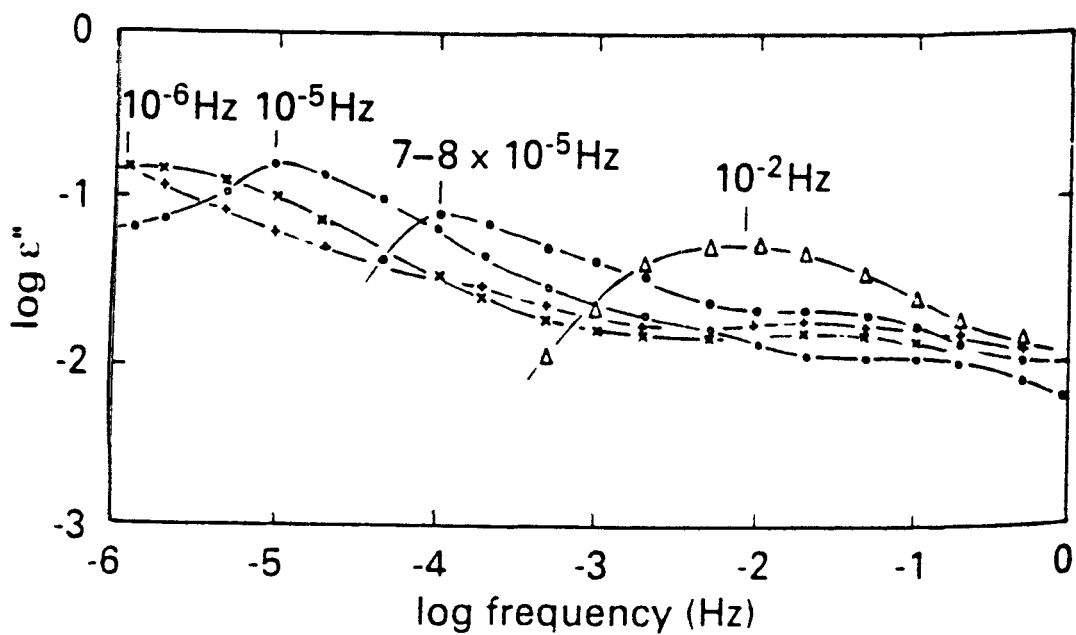


Fig. 6.24 Hamon transform results from desorption currents. Temperature ($^{\circ}\text{C}$) as shown. The peak at 39°C is outside the frequency window (Chohan et. al. 1995). (with permission of Chapman and Hall).

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